

ANALYSIS OF RESINS,
BALSAMS & GUM-RESINS

K. DIETERICH

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ANALYSIS OF RESINS

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ANALYSIS OF RESINS

BALSAMS AND GUM-RESINS

THEIR CHEMISTRY AND PHARMACOGNOSIS

*FOR THE USE OF THE SCIENTIFIC AND TECHNICAL RESEARCH
CHEMIST*

WITH A BIBLIOGRAPHY

BY

DR. KARL DIETERICH

OF THE HELFENBERG CHEMICAL WORKS

TRANSLATED FROM THE GERMAN

BY

CHAS. SALTER

LONDON

SCOTT, GREENWOOD & CO.

19 LUDGATE HILL, E.C.

1901

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D. VAN NOSTRAND COMPANY,

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PREFACE.

THE fact cannot be denied that the analytical data hitherto published with regard to the various resinous substances are far from being as uniform, accurate, and reliable as is the case with such bodies as the fats and oils for example. Even though the resins are, chemically speaking, in no way very similar, or nearly allied, to the definitely characterised fats, the great variations in the analytical values obtained are nevertheless remarkable, the methods of examination practised on the fats and oils having, almost without exception, been applied to the resins as well. Although, owing to the crude methods of preparation and diverse commercial usages, the constitution of the resinous substances—by which name the author implies the true resins, balsams, and gum resins—as inconstant, alterable mixtures of amorphous and, for the most part, unknown bodies, is such that no complete concordance of analytical values could be expected, it becomes an interesting, and indeed inevitable, problem to ascertain what are the causes of this lack of concordance; and an additional question also arises, namely, from what points of view should the matter be approached in future with the idea of improving the analytical method, and thereby securing greater uniformity in the results already obtained?

In the author's opinion, the relatively great fluctuations in existing results, which the reader will find recorded in the second part of the present work, are principally attributable to the following causes:—

- I. The methods employed.
- II. The use of extracts in place of the natural drugs.
- III. The lack of experiments conducted on authentic pure resins as they come from the parent tree, the results of which researches should constitute a basis of quality.
- IV. The lack of individuality in the resins examined, and which for the most part are not met with in an unadulterated state in commerce.

With regard to the first point, it may be said that almost every investigator has hitherto effected the saponification test by a different method. One has boiled the mixture under a reflux condenser, whilst another has allowed the alkali to act during a process of concentration; a third has restricted the operation to a short time, and a fourth extended it over a longer period. Similarly, no uniformity exists in the determination of the acid value, and a special method designed for general application to the resinous bodies in question is still wanting. Even though it be erroneous to employ a *single* uniform method for *all* resins—as has latterly been rightly attempted in the case of the fats and oils—and though it appears more advisable to specialise and individualise for each particular resin by itself, nevertheless a *uniform* method is necessary to enable all analysts to work according to well-defined conditions, and not in divergent ways, since slight deviations in the conditions of experiment are particularly liable to lead to great differences in the results when resinous substances are in question. Again, in connection with point II., it has hitherto been the practice of analysts to work exclusively with extracts and not with the natural drugs themselves. Now it is evident that no reliable opinion on the natural drugs can ever be based upon extracts, owing to the highly

divergent composition exhibited by these bodies (the gum resins particularly), in respect of their volatile constituents and substances soluble in alcohol, in consequence of which the saponification value of the extracts can never represent that of the crude products. Moreover, the extracts are so dark in colour that it is difficult to ascertain precisely the moment of change. To come to point III., the number of resinous products hitherto examined in a natural state, *i.e.* as they come from the parent plant, is very small, the commercial products being taken with all their impurities and modifications from the original types. Finally, in connection with point IV., it has been the custom to apply the methods of analysis used for fats and oils to the resinous bodies without taking the special constitution of the latter into consideration, and thus it is that determinations have been made of the ester value and saponification value of resins that contained no esters, acid value of non-acid resins, and so on. If, however, the pure scientific chemistry of the resins be regarded as the foundation for their analytical examination—as in the analysis of other substances—it becomes evident that the recent researches pursued in that subject by Tschirch, his pupils, and other workers, must be incentive to the revision, improvement, and individualisation of the methods of testing now in use for resins.

In this direction the author has endeavoured, by systematic investigation in the analysis of resins, to realise the conditions which he considers valuable for the improvement of the methods, and has hitherto laid down as fundamental rules for his own guidance, *viz.* :—

I. Analysing the natural drugs themselves.

II. Defining uniform regulations for the performance
of more rational methods.

- III. Individualising these methods, on the basis of the modern chemistry of the resinous bodies.
- IV. Selecting quantitative methods in preference to qualitative methods, the colour reactions in particular.
- V. Determining standard limits for the various constants, on the basis of investigations performed on authentically pure samples, taken direct from the parent tree.

Bearing these rules in mind, it will not be considered surprising that the author should have modified his method of determining the acid value (for example) to a different degree for almost every separate resin, the value being determined directly in one case, and indirectly, or in some other manner, in another. These modifications are not—as would at first sight appear—arbitrary, but are the result of practical experiments, intended to keep in touch with practice on the one hand, and the modern chemistry of the resins on the other.

Whether this method of procedure is correct or no, time will show. The author believes, nevertheless, that the present work will fill a gap in the literature of the subject, there being no comprehensive book as yet in existence dealing with the widespread researches in the domain of resin analysis, and because the space allotted to the author on this branch, in Lunge's work on chemico-technical methods of examination, was naturally very small, and insufficient to treat the available materials in anything like an exhaustive manner. At anyrate, the comprehensive data now published will contribute to the further development of the analysis of resins, and form a commencement for establishing definite value limits and methods, in so far as these data show the present state of the subject,

and the experience hitherto gained by workers in this branch.

If certain contradictions appear here and there in the experiences now published, reference thereto should not be construed as implying doubt as to the reliability of the authorities concerned, or as laying any blame on the latter, but solely as characterising the prevailing condition of things. It has already been stated that the uniformity of composition of the resins leaves much to be desired, and that external conditions, as well as the age of the sample, have considerable influence on the results of the analytical examination. This is especially true of such resins as dammar, copal, and sandarach, which exhibit oftentimes remarkable differences of solubility, even in the hands of unimpeachable authorities, according to the age and origin of the sample, and the length of time it has been exposed to air and light after exuding from the parent tree. Furthermore, when it is remembered that the acid saponification values are often empirical, and not theoretically unimpeachable, values, it will be evident what care must be bestowed on judging and appraising the available materials on the one hand, and how valuable on the other, to the subject of resin analysis, is a large accumulation of experimental, numerical data, and the experience connected therewith.

The prototype kept in mind by the author is the excellent work on *The Analyses of Fats and Waxes*, by Benedikt and Ulzer; the more so that Benedikt expressed the opinion that the analysis of the fats would prove instructive for the analysis of resins.

Although the analysis—*i.e.* testing and determining the value—of resins forms the main subject of the present work, it was also considered desirable to include the chemical and pharmacognostic data, necessary as a foundation, and to the

comprehension of their analysis, especially such of these data as correspond to the most recent state of knowledge. This portion has, however, been restricted to such points as concern the analysis and individualisation of the resins. The pure chemistry of the subject—the special sphere of labour of the Berne Institute, and its director, A. Tschirch—must naturally be reserved, as regards details, for the latter's work on *Resins and Resiniferous Substances*, shortly to be published.

The material at the author's disposal has been divided into two main portions—

Part I. General.

Part II. Special.

Of these, the first deals with the definition of the resins, the usual methods of examination, identification, classification, and general properties, as well as with the chemistry, etc., of the constituents of the resins; whilst the second part treats of the resins separately, and describes their—

Origin and habitat.

Chemical constituents on the basis of recent research.

General properties and commercial varieties.

Adulterations and substitutions.

Analysis and evaluation.

Literature, referring solely to analysis, in order to facilitate the consultation of the original reports.

In using this special part for the analytical testing of resins, special attention is directed to the Introduction, the General Remarks, and Definitions, and, above all, to the Abbreviations given for the constantly recurring factors, such as the acid, ester, and saponification values. These abbreviations have been systematically arranged in such a manner as to also indicate the method of determination employed. Thus, for instance, S.-Z. d. and S.-Z. ind. refer to the acid values determined respectively by the

direct and indirect (back titration) methods. The S.-Z. f. is the acid value of the volatile constituents. V.-Z. h. and V.-Z. k. indicate hot and cold saponification values, thus showing at once—as already proposed in connection with the analysis of fats—which method furnished the values set forth. The main object of strictly adhering to these abbreviations in this special section of the work, is to bring these practical symbols into general use. In addition, a brief notice of the method is given in each case, with particular information as to whether the natural product or only a portion (alcoholic extract in alcoholic solution, etc.) of the resin was examined.

The calculation of the values found by the author's own methods has been carried out on the basis of the table of atomic weights determined recently by Landolt, Ostwald, and Seubert, and accepted by the German Chemical Society.

Where practicable, colloquial nomenclature has been adopted for the various resins instead of the Pharmaceutico-Latin names, though the latter have been retained in such cases as galbanum, ammoniacum, where no colloquial term has come into general use.

There being as yet no thorough classification possible on purely chemical lines, the subdivision into—

- A. Balsams,
- B. Resins,
- C. Gum Resins,

has been retained in the special part.

An Appendix has been added, embodying all the recent investigations published while the book was in course of printing, and which, together with a few necessary supplementary remarks, it was found desirable to include. Special attention has been bestowed on the Index.

Finally, it is the author's welcome duty to record his thanks to those who have given assistance to his task. This applies, in the first place, to his chief assistant—of many years' standing—Mr. H. Mix, who has rendered valuable service in collecting literary matter, reading proofs, and in numerous practical researches, etc. Furthermore, thanks are due to Professor Dr. A. von Vogl, who was good enough—through the kind mediation of Mr. A. Kremel—to enrich the author's collection of resins by exchanges with the Viennese pharmacognostical collection; also, to Messrs. Gehe & Co. (Dresden), Worlée & Co. (Hamburg), and E. & H. Oldendorf (London), for having kindly supplied, for examination, numerous samples of rare resins or commercial varieties.

It is hoped that the present work will meet with a good reception, as forming a decided contribution towards the characterisation of the resinous bodies; and that the collaboration of colleagues will enable a second edition to record real progress and improvement in the analytical examination of these bodies—progress that will bring us soon to the goal of resin analysis, viz. *the definite establishment of rational methods and limits of valuation for the constants*.

KARL DIETERICH.

HELFENBERG, *January* 1900.

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ABBREVIATIONS.

<i>A. d. Ph.</i>	= Archiv der Pharmacie (Schmidt and Beckurts).
<i>Ph. C.</i>	= Pharmaceutische Centralhalle (A. Schneider).
<i>Ph. Ztg.</i>	= Do. Zeitung (Böttger).
<i>Chem. Rev.</i>	= Chemische Revue über die Fett- und Harz-Industrie (R. Henriques).
<i>H. A.</i>	= Helfenberger Annalen (K. Dieterich).
<i>Ch. Ztg.</i>	= Chemiker Zeitung (Krause).
<i>Ap. Ztg.</i>	= Apotheker Zeitung (Salzmann).
<i>Südd. Ap. Ztg.</i>	= Süddeutsche Apotheker-Zeitung (Kober).
<i>Oest. Ch. Ztg.</i>	= Oesterreichische Chemiker Zeitung (Heger).
<i>Ph. P.</i>	= Pharmaceutische Post (Heger).
<i>N. z. P. d. A.</i>	= Notizen zur Prüfung der Arzneimittel, 1889 (Kremel).
<i>D. d. H. A.</i>	= Decennium der Helfenberger Annalen (E. Dieterich).
<i>R. E.</i>	= Real Encyclopædia (Geissler-Möller).
<i>I. D.</i>	= Inaugural Dissertation.
<i>Ap. Ztg. R.</i>	= Apotheker Zeitung: Repertorium.
<i>D. A. III.</i>	= Deutsches Arzneibuch (German Pharmacopœia), 3rd Edition.

ANALYSIS OF RESINS.

PART I.

GENERAL.

Definition of Resins in General.—The terms “resin” and “resinous substance” generally imply certain secretion products of plants, excreted, in the course of metabolism, partly as a normal phenomenon, partly as the outcome of disease.

Whereas, formerly, the resins were regarded as conversion products of the tannic acids and phlobaphenes, or even as precursors of the ethereal oils (Dragendorff¹), the tendency nowadays is rather to consider the phlobaphenes as oxidation products of glucoside resinotannic acids, and the resins as oxidation products of the ethereal oils. According to Wallach the terpenes in particular appear to stand in a certain relation towards these secretions. As to what substances are actually drawn upon in the plant in order to form resins no definite conclusion is as yet possible. That oxidation processes play a great part, both in the plant before and after exudation of the secretion, and also after the collection and storage² of the same in contact with air and light, has

¹ *A. d. Ph.*, 1879, vol. 15 p. 50.

² See Kiessling, Weger, and Lippert, on “Oxygen Absorption by Resins”: *Chem. Rev.*, 98, I. 286; *Zeits. f. angew. Chem.*, 98, I., 1248; and Weger's pamphlets published in 1899 (Baldamus, Leipzig).

recently been made clear by K. Dieterich,¹ with examples. According to this report, the resins and resinous products that come into our hands are, for the most part, merely secondary products, differing widely from the excretion products and products of the degradation of high molecular compounds, as constituted within the tree or at the moment of exudation. Consequently, before reaching our hands as commercial products, the resins have really passed through three stages of modification, in each of which phases certain different influences have differently modified the composition of the mixtures. The secretion, while inside the tree, will, as the primary stage, exhibit a very different composition to what it does after exudation and exposure to air and light—a change externally evidenced by the hardening of the product and by its altered colour. The following manipulations in the recovery of these products—melting, extracting, etc.—then cause further changes, the result of which is that commercial resins are really secondary and tertiary mixtures. Consequently, as mentioned in the Preface, it is of particular importance to the attainment of a knowledge of the resins that authentically pure samples, taken direct from the parent plant, should be examined, in order that rational methods of testing, and normal values, may be established. Unfortunately this has hitherto been impossible, except in the case of very few resins and balsams (Peru balsam, benzoin, storax, etc.). That, in any event, the resins—in opposition to the fats, which are mostly synthetical products—should be regarded as oxidation and condensation products, and, in fact, as degradation products of high molecular compounds, by oxidation, or as condensation products of high molecular compounds, is proved—to give only a limited number of examples—on the one hand, by the earlier attempts at the artificial synthesis

¹ *H. A.*, 1896, pp. 15 *et seq.*

of resins from Venice turpentine and fuming sulphuric acid (Voges, especially in the preparation of artificial incense); further, from ethereal oils and anhydrous phosphoric acid (Hlasiwetz); the artificial preparation of caoutchouc from turpentine oil and gaseous hydrochloric acid; and, on the other side, the condensation experiments of Döbner and Lückner for the production of an artificial guaiacum resin, as also the condensation experiments of A. von Bayer for preparing undefined resinous products from aldehydes and phenols.

From the physical aspect we apply the terms "resin" and "resinous substance" to such products as exhibit an amorphous (rarely a crystalline) structure, are sticky and fusible, burn with a smoky flame, are mostly or entirely insoluble in water, and—unlike the fats and oils—leave no greasy streak on paper; are saponifiable, not liable to rancidity, and constitute mixtures of various coloured and colourless, solid and liquid, aromatic and inodorous constituents. Since the number of uniform products, such as colophony ("resin"), which contains resin alone, without any gums, ethereal oils, or any large proportion of other important constituents, is small, the general term "resin" has been applied to a large number of mixtures, which, being aggregations of the pure substance with vegetable and mineral impurities, are distinguished by the names—Balsams, Gum Resins, and True Resins. In fact, nowadays, some go so far as to include with the resins certain vegetable saps, such as aloes and catechu, containing only a relatively small proportion of resin.

Definition of the Balsams, and especially the Gum Resins.—By *balsams* we understand such resinous mixtures as contain the resin dissolved or emulsified in ethereal oils, are more or less fluid, and usually exhibit a strong,

specific odour. *Gum resins* are mixtures of such bodies as gums, extracts, bitter principles, resin, etc., which, being in themselves only partially soluble, give up certain parts to water, and partly contain ethereal oils, in addition to resin and gums, their consistence varying according to the composition.

External and Superficial Characteristics of Resinous Bodies.—Wiesner¹ thoroughly investigated this question, and found that the condition of the surface is influenced by solidification or weathering, or the two conjoined. Thus the “goose skin” of copal is due to weathering. In the gum resins—Flückiger’s opinion notwithstanding—no homogeneity of surface or admixture is present, but they mostly consist of gums enclosing droplets of resin and oil. Thus gamboge, for example, is a hyaline mass with embedded drops of resin and oil. With regard to the individual types (gamboge, ammoniacum, and galbanum type; asafoetida, olibanum, and myrrh type) and special individuals, see Wiesner (*l.c.*).

Distinction between Resinous Bodies and the Fats and Oils.—As already mentioned, the resins differ from the fats and oils even in their origin. The fats are mostly of synthetic origin, the resins formed generally by degradation or condensation. Whereas the fats and oils, as glycerides of the fatty acids, constitute substances of definite character, the resinous bodies are variable and impure mixtures of substances that for the most part are unknown.

Furthermore, it is noteworthy that in the hydrolytic decomposition of the fats and oils, which represent esters of the fatty acids, the acids are obtained in excess whilst the alcohols (glycerin) are in smaller quantity. On the other hand, the esteriferous resins corresponding to the fats mostly yield but very small amounts of aromatic or resin acids, with

¹ *Zeits. d. Allgem. Oestr. Apoth.-Ver.*, 1899, Nos. 16 and 18.

a far larger proportion of alcohols (resinols and resinotannols). However, despite these great genetic and chemical differences, the methods employed for the examination of the oils and fats have, almost without exception, been successfully applied to the resinous substances as well.

Origin, Occurrence, and Collection of Resinous Substances.—These bodies, as already remarked, are secretions, *i.e.* excretory products from resiniferous trees and plants, and exude to some extent naturally therefrom as a physiological phenomenon, though for the most part they are collected as a result of pathological treatment by man. According to the researches of Tschirch, Möller, and others, nearly all the resins, gum resins, and balsams are formed in special secretory glands; the solid resins, such as furnished by the *Umbelliferae*, *e.g.* asafœtida, ammoniacum, etc., being exuded by the epithelial cells into the so-called chizogenic glands, whilst the balsams are formed in the lysigenic oil cavities by the dissolution of the cell membranes. Just as external treatment by the hand of man is able to convert the physiological excretion of the resins into a pathological phenomenon, a similar excessive pathological secretion, *e.g.* the malady of “gummosis” in certain gum trees, may occur in the absence of external influences. Particularly numerous and important resinous products—gum resins especially—are furnished by the *Umbelliferae* and *Burseraceae*, and the varieties *Pinus* and *Larix* also yield a large number of resins, whilst we are indebted to the *Casalpinaceae* for some very important balsams. Few of the resiniferous trees are indigenous to Europe, whereas America supplies a great many resinous products, as also Africa and Asia—Persia and Asia Minor especially. Of the gum resin trees none to speak of are indigenous, and but few resins, such as pine resin, turpentine, and one or two others; and this lack of material at first hand is a great drawback

to the attainment of accurate information on the collection, original composition, and real origin of the resins, all of which points still remain to some extent in obscurity. Finally, when it is borne in mind the great distances and large number of hands through which these bodies have to pass, it will cease to be surprising to find that the products reach us in a totally altered, variable, and, above all, adulterated condition. So far as the methods of collecting resins are concerned, such as cutting the trees, boiling the twigs and branches, concentrating the extract, etc., these are so crude and variable that the resulting products can hardly help exhibiting irregularities in their properties, etc.

Classification.—On the basis of physical properties the resinous substances can be classified into balsams, resins, and gum resins. And at the present time, when the chemistry of these bodies is by no means complete, although progressing, and when only such resins as have been more closely investigated can be subjected to chemical classification, the physical method remains the most accurate and practical, notwithstanding its lack of absolute precision and the frequent occurrence of intermediate members and transition grades. Up to a certain extent chemical classification has been rendered possible by the classical and systematic labours of Tschirch and his pupils, at least so far as concerns the resin products hitherto subjected to careful examination; and the following classification has been proposed by K. Dieterich on the basis of Tschirch's investigations:—

1. Resins which consist of esters of the aromatic series, and either contain free acids or not—*e.g.* benzoin, dragon's-blood, acaroid resin, etc.
2. Resins consisting of esters of special resin acids, and containing, in addition, free resin acids or not—*e.g.* turpentine, mastic, succinite, elemi, etc.

3. Resins which are not esters, but contain only free resin acids, occasionally accompanied by inert admixtures. To this class belong colophony, copal, guaiacum, sandarach, dammar, etc.

In addition, the author also proposed to group the resinous substances according to the mode of collection pursued, *i.e.* natural (physiological excretion) and artificial (pathological excretion).¹ To the first group would belong all such resins as—like dragon's-blood—exude naturally from the tree without human interference; and to the other class, all such as are collected by wounding, heating, etc.,—the quantities so obtained being far greater than those recoverable by the natural method. This latter category, nowadays, comprises nearly the entire series of the resins, artificial means being necessarily resorted to for the systematic collection of these bodies.

Fr. Lewton would classify the resinous substances as follows:²—

TRUE RESINS.—Vegetable substances, hard, pulverulent, resembling gum in outward appearance, neither soluble in, nor softened by, cold water. They burn with a light, smoky flame, and contain much C, little O, and no N.

Chemical composition difficult to define; usually mixtures of resin acids.

Sub-groups :—

(*a*) Copal group.—These will not dissolve in the usual solvents unless themselves previously fused.

(*β*) Dammar group.—More or less soluble in ether,

¹ *H. A.*, 1896, pp. 33 *et seq.*

² It should be stated that this classification, based on physical and chemical characteristics, is not altogether free from objection; furthermore, that the characteristics based on solubility do not quite coincide with present day experience. The table is reproduced here for the sake of completeness, and as being worthy of attention, despite sundry deficiencies.

chloroform, benzene, acetone, turpentine oil, etc., but quite insoluble in alcohol.

(γ) Sandarach group.—More or less soluble in alcohol without the application of heat. Guaiacum also belongs to this group.

(δ) Colophony group.—Entirely soluble in alcohol.

(ϵ) Benzoin group.—Soluble in alcohol. Liberate benzoic or cinnamic acid when heated.

(θ) Shellac group.—Resinous excretions caused by insect punctures. Form a turbid solution in alcohol.

INODOROUS GUM RESINS.—Vegetable excretions, destitute of volatile oils, and consisting of variable mixtures of gums and resin. They furnish an emulsion with water. Gamboge belongs to this class.

AROMATIC GUM RESINS.—Like the above, but contain ethereal oils.

Sub-groups :—

(α) Asafoetida group.—Mostly derived from umbelliferous plants, and give off a disagreeable smell. In addition to asafoetida, the group comprises galbanum, ammoniacum, and opopanax.

(β) Myrrh group.—These have a more or less agreeable aroma, and are, for the most part, derived from the *Burseraceæ*. Examples: Myrrh, olibanum, bdellium.

OIL RESINS.—Vegetable excretions, consisting of resins and volatile oils, the former being frequently in solution in the latter, and therefore liquid.

Sub-groups :—

(α) Varnish group.—Produce a shiny coating when applied to any surface. Mostly derived from plants of the *Anacardiaceæ* family.

(β) Copaiba group.—Sweet-smelling liquids, mostly

classified with the balsams, but differing therefrom by containing less resin.

(γ) Turpentine group.—Comprises the soft resins, containing larger or smaller amounts of volatile oils. Derived from *Coniferae*.

(δ) Elemi group.—Soft resins, rarely containing above 10 per cent. of ethereal oil. Derived from *Burseraceae*.

TRUE BALSAMS.—Vegetable excretions, consisting of resin, aromatic acids, alcohols, and esters. Examples: Peruvian balsam, Tolu balsam, and liquid storax.

Chemical Constituents of Resinous Substances.—With regard to these and their characteristics, the main features have been recorded by Tschirch¹ as follows:—

1. He finds the main constituents to be—

- (a) Resin esters (resins) or their products.
- (b) Resin acids (resinolic acids).
- (c) Resenes, indifferent bodies of unknown classification.

Very few resins contain representatives of all three groups, the majority being either ester resins, resinolic acid resins, or resene resins.

Aroma, when present, is influenced by ethereal oils, aldehydes, or very small quantities of liquid esters, among which cinnamic acid esters, and especially the phenylpropyl ester of this acid, play a part.

2. The aromatic acids forming resin esters, or resins, appear to be mutually related, and are divisible into two classes, one of which starts with benzoic acid, and the other from cinnamic acid.

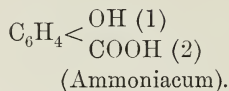
¹ In view of the circumstance that Prof. Tschirch is bringing out a work on resins and resiniferous plants, which will deal with the chemistry of the subject, the present author confines himself to a brief résumé of Tschirch's researches, and refers the reader to that authority's own book for fuller details.

I. Benzoic acid: C_6H_5COOH (Peruvian balsam, Tolu balsam, Siam benzoin, dragon's-blood).

Benzoylactic acid :

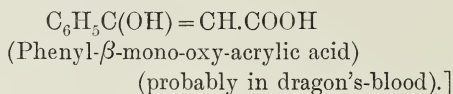


Salicylic acid :

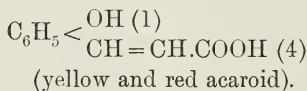


II. Cinnamic acid: $C_6H_5.CH=CH.COOH$ (Tolu balsam, Peruvian balsam, storax, Sumatra benzoin, yellow acaroid resin).

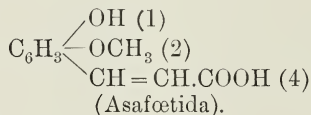
[β -Phenylhydracrylic acid :



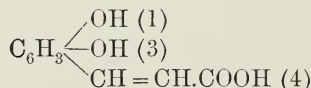
p-Cumaric acid :



Ferulaic acid :



Umbellic acid :



and its anhydride, umbelliferon (in asafoetida, galbanum, saganum).

The aromatic acids forming resin esters are therefore mostly oxyacids. Of the fatty acids only the resin ester of succinic acid (amber) has hitherto been observed.

3. The resin alcohols forming resin esters are either colourless: resinols—in which case they do not give the tannin reaction;—or are coloured, and answer to the tannin reaction: resinotannols.

A. Resinols.—Four members of this series are known :—

Succinoresinol : $C_{12}H_{20}O$, in amber (Tschirch and Aweng).

Storesinol : $C_{12}H_{20}O$, or $C_{36}H_{58}O_3$, in storax (von Miller).

Benzoresinol : $C_{16}H_{25}(OH)O$, in benzoin (Tschirch and Lüdy).

Chironol : $C_{28}H_{47}(OH)$, in burs. opopanax (Tschirch and Baur).

Amyrine ($C_{30}H_{49}OH$) may also belong to this series.

Of the resinols, storesinol is certainly allied to benzo-resinol, the spectrum analysis of the solutions in concentrated sulphuric acid placing this beyond doubt. If the simple formula be taken as a basis there is absolutely no difference in percentage composition between succinoresinol and storesinol. Hence these substances are apparently related to one another. All the resinols belong to the aromatic series.

B. Resinotannols.—The following are known :—

Siaresinotannol : $C_{12}H_{13}O_2(OH)$, in Siam benzoin (Tschirch and Lüdy).

Sumaresinotannol : $C_{48}H_{19}O_3(OH)$, in Sumatra benzoin (Tschirch and Lüdy).

Peruresinotannol : $C_{18}H_{19}O_4(OH)$, in Peruvian balsam (Tschirch and Trog).

Toluresinotannol : $C_{17}H_{17}O_4(OH)$, in Tolu balsam (Tschirch and Oberländer).

Galbaresinotannol : $C_{18}H_{29}O_2(OH)$, in galbanum (Tschirch and Conrady).

Ammoresinotannol : $C_{18}H_{29}O_2(OH)$, in ammoniacum (Tschirch and Luz).

Sagaresinotannol : $C_{24}H_{27}O_4(OH)$, in sagapenum (Tschirch and Hohenadel).

Dracoresinotannol : $C_8H_9O(OH)$, in palm dragon's-blood (Tschirch and K. Dieterich), $C_{24}H_{30}O_4$.

Panaxresinotannol : $C_{34}H_{49}O_7(OH)$, in burs. opopanax (Tschirch and Baur), $C_{17}H_{25}O_4$.

Xanthoresinotannol : $C_{43}H_{46}O_{10}$, in yellow acaroid (Tschirch and Hildebrand).

Erythroresinotannol : $C_{40}H_{40}O_{10}$, in red acaroid (Tschirch and Hildebrand).

On looking over these formulæ, the first thing to strike the eye is that six of the resinotannols contain multiples of six carbon-atoms—Siaresinotannol, sumaresinotannol, peruresinotannol, galbaresinotannol, ammoresinotannol, and saguesinotannol.

Probably dracoresinotannol belongs to this series as well. Furthermore, it is evident that galbaresinotannol and ammoresinotannol have the same percentage composition, and that peruresinotannol differs from sumaresinotannol by merely a single oxygen atom. There are, however, other points of resemblance. Thus peruresinotannol is a homologue of toluresinotannol (differing only by a surplus of CH_2), and xanthoresinotannol seems to be a homologue of erythroresinotannol, the difference amounting to 3 CH_3 . Similarly, relationships exist between saguesinotannol and xanthoresinotannol; and probably panaxresinotannol also belongs to the group with 18, or 17, carbon atoms. Finally, it can be seen that all the resinotannols contain only a single hydroxyl in the molecule. The readiness with which picric acid is formed when the resinotannols are treated with nitric acid, rather indicates that this HO is connected with a benzene nucleus and not with one of the side chains, *i.e.* is cyclostatic, not streptostatic. Picric acid is most readily formed from the tannols of acaroid resin, though all the others also yield the same product without difficulty. In the case of ammoresinotannol and saguesinotannol, styphnic acid (trinitroresorcin) is obtained, whilst galbaresinotannol furnishes camphoric acid and camphoronic acid. When fused with potash, fatty acids appear, and in some cases protocatechuic acid, or resorcin, is formed. The resinotannols, therefore, also belong to the aromatic series.

4. The *resin acids* or *resinolic acids*, which chiefly occur in the free state in resins, are, so far they have been investigated, all oxyacids, *i.e.* contain hydroxyl and carboxyl. Their composition is as follows:—

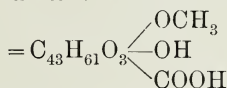
Podocarpic acid : $C_{17}H_{22}O_3$, in podocarpin resin (Oudemans).

Abietic acid : $C_{44}H_{64}O_5$, in colophony (Maly). According to Mauch the formula is $C_{19}H_{28}O_2$.

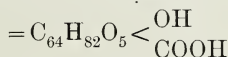
Pimaric acid : $C_{20}H_{30}O_2$, in pine resin (Maly).

Succinoabietic acid : $C_{80}H_{120}O_5$, in amber (Tschirch and Aweng).

Sandaracolic acid : $C_{45}H_{66}O_7$, in sandarach (Tschirch and Balzer).



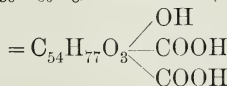
Callitrolic acid : $C_{65}H_{84}O_8$, in sandarach (Tschirch and Balzer).



Trachylolic acid : $C_{56}H_{88}O_8$, in copal (Tschirch and Stephan).

Isotrachylolic acid : $C_{56}H_{88}O_8$, in copal (Tschirch and Stephan).

Dammarolic acid : $C_{56}H_{80}O_8$, in dammar (Tschirch and Glimmann).



Guaiacic acid : $C_{20}H_{26}O_4$, in guaiacum (Hlasiwetz).¹

Guaiaconic acid : $C_{19}H_{20}O_5$, in guaiacum (Hadelich).

Copaibic acid : $C_{20}H_{30}O_2$, in copaiba balsam (Schweitzer).

The other acids in copaiba and elemi also probably belong to the resinolic series.

Certain relations appear to exist among the resin acids. Thus the only difference between trachylolic acid, its isomers, and dammarolic acid is one of eight hydrogen atoms, so that the first named may be regarded as to some extent an orthohydrodammarolic acid; and sandaracolic acid can, on the basis of Maly's formula, be considered as a homodioxyabietic acid. That furthermore, succinoabietic acid is allied to abietic acid may also be presumed from a comparison of the formulæ, all that is necessary being to double that of the last-named acid. Again, the acids in guaiacum appear to be related to one another and also to copaibic acid and pimaric acid. If

¹ These reports on guaiacic acid have been recently modified by the labours of Döbner, Lütcker, Herzig, and Schiff.

Mauch's formula for abietic acid be taken as the basis, then pimaric acid is homoabietic acid, and abietic acid becomes still more closely connected with copaibic acid and the acids of guaiacum.

Still closer relationship seems to exist between succinoabietic acid and pimaric acid. If the formula of the latter be multiplied fourfold, it may be considered as a heptoxysuccinoabietic acid, and copaibic acid corresponds exactly, in percentage composition, with pimaric acid. Only a single hydroxyl radicle can be detected in any of the resin acids; but whereas some of them contain only one carboxyl (sandaracolic acid, podocarpic acid), others have two (dammarolic acid, trachylolic acid, succinoabietic acid, and abietic acid.)

A noteworthy circumstance is the relatively great resistance offered by many resinolic acids to potash in a state of fusion, as also the fact that both abietic acid and succinoabietic acid furnish succinic acid when fused with potash.

5. The *resenes* undoubtedly form the most difficult class of the constituents of resin, and their resistance towards the majority of reagents renders their classification impossible for the present. They are neither hydrocarbons nor alcohols, acids, esters, ketones, nor aldehydes, but, so far as they have been examined, appear to belong to the aromatic series. They are all insoluble in potash. This resistance, however, is just the quality that places them for practical purposes among the most valuable constituents of the resins,¹ since the value of a resin in practice is so much the higher in proportion to its power of resisting manifold attacking influences. The following resenes are known:—

¹ Hence we find the resins employed for varnish-making, *e.g.* copal, dammar, dragon's-blood, etc., contain relatively large amounts of resenes. Whether this is a predominant factor in determining their value, and a quantitative examination is desirable, is a matter that would repay attention and prove of interest to the valuation of copal, etc.

α -Panaxresene: $C_{32}H_{54}O_4$, in burs. opopanax (Tschirch and Baur).

β -Panaxresene: $C_{32}H_{52}O_5$, in burs. opopanax (Tschirch and Baur).

α -Dammarresene: $C_{33}H_{52}O_3$, in dammar (Tschirch and Glimmann).

β -Dammarresene: $C_{31}H_{52}O$, in dammar (Tschirch and Glimmann).

Fluavil: $C_{40}H_{64}O_4$, in gutta-percha (Tschirch and Oesterle).

Alban: $C_{40}H_{64}O_3$, in gutta-percha (Tschirch and Oesterle).

α -Copalresene: $C_{25}H_{38}O_4$, in copal (Tschirch and Stephan).

Dracoalban: $C_{20}H_{40}O_4$, in palm dragon's-blood (Tschirch and K. Dieterich).

Dracoresene: $C_{26}H_{44}O_2$, in palm dragon's-blood (Tschirch and K. Dieterich).

Myroxoresene: $C_7H_{10}O$, in the fruit of myroxylons (Tschirch and Germann). $C_{21}H_{30}O_3$.

That the two panaxresenes are allied is seen by comparing their formulæ. The β -panaxresene is apparently an oxidation product of the α -resene. The same applies to fluavil and alban, as also to the dammarresenes. Moreover, a close relationship probably exists between the panaxresenes and the dammarresenes, as also between fluavil and alban on the one hand, and α -copalresene on the other.

In addition to the above-named resins, Tschirch has also investigated asafœtida, guaiacum, olibanum, aloe resin, shellac, bisabol myrrh, opopanax (from *Umbelliferae*), etc.; and the same authority has compiled the following table of resins obtained from *Burseraceæ*:—

[TABLE.

	Resin Acids.	Resenes.	Ethereal Oil.	Gum.	Bassorin.	Bitter Principle.
Bdellium						
Elemi	59% resin Elemic acid : $C_{35}H_{46}O_4$ Amyrin $C_{25}H_{42}O$ Bryoidin $C_{20}H_{38}O_3$	60-70% amorphous resin α -Resene : $C_{11}H_{17}O$ β -Resene : $C_{31}H_{52}O$ Masticin : $C_{20}H_{32}O$	not investigd. ($C_{10}H_{16}$) ⁿ Dipentene Phellandrene not investigd.	not inv. — — —	not inv. — — —	not inv. — not inv. —
Dammar (Tschirch and Glimmann) Mastic	Dammarolic acid : $C_{56}H_{80}O_8$ Masticinic acid : $C_{20}H_{32}O_2$	Absence of esters alone determined.	$C_{10}H_{16}$ Pinene	—	—	—
Mecca balsam (Tschirch and Baur) Myrrh (Köhler)	$C_{13}H_{16}O_8$ (2 bas.) $C_{26}H_{32}O_9$ (2 bas.) 2 free, 2 combined, one being ($C_9H_{13}O_2$) ⁿ	$C_{23}H_{34}O_5$ ($C_{29}H_{47}O_6$) ⁿ	$C_{10}H_{14}O$ $C_{10}H_{16}$	$C_8H_{10}O_5$ (57-59%) not inv.	— not inv.	— not inv.
Bisabol myrrh (Tucholka) Olibanum (Tschirch and Halbey)	Boswellic acid : $C_{32}H_{52}O_4$, partly as an ester.	Olibanoresene : ($C_{14}H_{22}O$) ⁿ	($C_{10}H_{16}$) ⁿ Pinene, dipentene, phellandrene, cadinene	$C_8H_{30}O_5$ Arabic acid	not inv. not inv.	not inv.
Bur ^s . opopanax (Tschirch and Baur)	Chironolic acid : $C_{38}H_{48}O_4$ from Chironol : $C_{28}H_{48}O$ Panaxresinotanol : $C_{34}H_{50}O_8$	α -Panaxresene : $C_{32}H_{54}O_4$ β Panaxresene : $C_{32}H_{52}O_5$	not investigd.	not inv.	not inv.	not inv.

Author	Tannol	Formula	% C	% H	Acetylation	Benzoylation	Treatment with HNO_3	Potash fusion test
Tschirsch and Pedersen (Aloe)	Aloresinotannol	$\text{C}_{22}\text{H}_{36}\text{O}_6$	68.39	6.73	—	$\text{C}_{22}\text{H}_{24}\text{O}_6(\text{C}_6\text{H}_5\text{CO})_2$	—	—
Tschirsch and Luz (Ammoniacum)	Ammonresinotannol	$\text{C}_{18}\text{H}_{30}\text{O}_3$	73.45	10.20	$\text{C}_{18}\text{H}_{26}\text{O}_3 \cdot \text{CH}_3\text{CO}$	$\text{C}_{18}\text{H}_{26}\text{O}_3(\text{C}_6\text{H}_5\text{CO})$	Styphnic acid	Resorein
Tschirsch and Polasek (Asafetida)	Asaresinotannol	$\text{C}_{24}\text{H}_{34}\text{O}_5$	71.43	8.69	$\text{C}_{24}\text{H}_{33}\text{O}_5 \cdot \text{CH}_3\text{CO}$	$\text{C}_{24}\text{H}_{33}\text{O}_5(\text{C}_6\text{H}_5\text{CO})$	Picric acid	—
Tschirsch and Lüdy (Sumatra benzoin)	Sumaresinotannol	$\text{C}_{18}\text{H}_{30}\text{O}_4$	72.00	6.66	—	—	Picric acid	Protocate- chuic acid
Tschirsch and Lüdy (Siam benzoin)	Siaresinotannol	$\text{C}_{12}\text{H}_{14}\text{O}_3$	70.01	7.01	$\text{C}_{12}\text{H}_{13}\text{O}_3 \cdot \text{CH}_3\text{CO}$	—	Picric acid	—
Tschirsch and Conrady (Galbanum)	Galbaresinotannol	$\text{C}_{18}\text{H}_{30}\text{O}_3$	73.45	10.22	$\text{C}_{18}\text{H}_{26}\text{O}_3 \cdot \text{CH}_3\text{CO}$	$\text{C}_{18}\text{H}_{26}\text{O}_3(\text{C}_6\text{H}_5\text{CO})$	Camphoric and Camphor- onic acids	—
Tschirsch and Baur (Burs. opopanax)	Panaresinotannol	$\text{C}_{34}\text{H}_{50}\text{O}_8$	69.62	8.53	—	—	—	—
Tschirsch and Trog (Peru balsam)	Peruresinotannol	$\text{C}_{18}\text{H}_{30}\text{O}_5$	68.30	6.30	$\text{C}_{18}\text{H}_{19}\text{O}_5 \cdot \text{CH}_3\text{CO}$	$\text{C}_{18}\text{H}_{19}\text{O}_5(\text{C}_6\text{H}_5\text{CO})$	Oxalic and Picric acids	—
Tschirsch and Knitl (Umb. opopanax)	Oporesinotannol	$\text{C}_{12}\text{H}_{14}\text{O}_3$	69.83	6.33	—	$\text{C}_{12}\text{H}_{13}\text{O}_3(\text{C}_6\text{H}_5\text{CO})$	Oxalic and Picric acids	—
Tschirsch and Hohen- adel (Sagapenum)	Sagaresinotannol	$\text{C}_{24}\text{H}_{38}\text{O}_5$	72.70	7.07	$\text{C}_{24}\text{H}_{27}\text{O}_5 \cdot \text{CH}_3\text{CO}$	$\text{C}_{24}\text{H}_{27}\text{O}_5(\text{C}_6\text{H}_5\text{CO})$	Styphnic acid	—
Tschirsch and Ober- länder (Tolu balsam)	Toluresinotannol	$\text{C}_{17}\text{H}_{18}\text{O}_5$	67.50	5.96	$\text{C}_{17}\text{H}_{17}\text{O}_5 \cdot \text{CH}_3\text{CO}$	$\text{C}_{17}\text{H}_{17}\text{O}_5(\text{C}_6\text{H}_5\text{CO})$	Picric and Oxalic acids	Protocate- chuic acid

The foregoing results point to a fairly general concordance in the composition of the drugs in question; and, compared with other groups, a complete retirement of esters and alcohols, whilst the resin acids and resenes, together with the gums, form the main constituents. Specially noteworthy is the approximation of the empirical formulæ of boswellic and chironolic acids, and still more so that of the α - and β -panaxresenes.

A comparative table (see preceding page) of the chief resinotannols has also been compiled by Tschirch.

Finally, mention may be made of an interesting tabulation by Halbey of the behaviour of the constituents of resin towards the cholesterin reactions, the results being all the more interesting from having been obtained with the *pure substances*, and not the crude mixtures; hence the colour reactions may be regarded as perfectly reliable. Recently also, K. Dieterich has recommended working with the isolated resin acids and alcohols in quantitative estimations, in the same way as adopted for fats; since just as certain reactions of oils and fats are characteristic for the corresponding pure constituents alone, so the investigation of the isolated constituents of resins may lead to better concordance in the resulting values. The cholesterin reactions are given in the subjoined tables.

On the basis of the oxidation, reduction, and fission products of the substances hitherto found in resins, and also of the potash-fusion test,¹ the resins and their constituents may be regarded, almost without exception, as aromatic, and not aliphatic, derivatives.

Whereas nitrogenous bodies are rarely, if ever, found in the gum resins, balsams, and resins, sulphur compounds

¹ See Wiesner and Hlasiwetz, *Die technisch verwertheten Balsame, Harze, und Gummiharze*, 1869, pp. 70 *et seq.*, 81-84.

are more frequent, *e.g.* in asafœtida, succinite, and sagapenum. It is one of the main advances made in the modern chemistry of resins that substances formerly looked upon as uniform have now been separated into several well-defined constituents. To these results—a valuable success attained by Tschirch and his pupils—we are indebted for a further advantage, *viz.* the possibility of more uniform nomenclature for the resins; and the names introduced by Tschirch, such as resins, resinols, resinotannols, resinolic acids, resenes, etc., are now well known and adopted generally.

[TABLE.

Behaviour of Resin Constituents towards the Cholesterin Reactions.

Substance.	Formula.	Analyst.	Melting-point.	Hesse's Reaction.		Drop Coloration in the Porcelain Basin.	Liebemann's Reaction.
				CHCl ₃	H ₂ SO ₄		

Substances imparting a deep Red coloration to Chloroform in Hesse's Test.

Cholesterin	$C_{26}H_{44}O + H_2O$	Mauthner	148.5° C.	blood red	pale yellow	blue, green, yellow	red, blue, green
Phytosterin (from grass leaves)	$C_{26}H_{44}O + H_2O$	Tschirch	132-133°	cherry red	pale yellow	blue, green, yellow	red, blue, green
Lanolin	—	—	—	red-brown	yellow	blue, green, yellow	yellow, green
Myroxin	$C_{29}H_{46}O$	Tschirch and Germann	—	blood red	pale yellow	dirty green, yellow	faint reddish
Dracoalban	$C_{29}H_{46}O_4$	Tschirch and K. Dieterich	—	red-brown	yellow	dirty green, yellow	red, brown-red
Olibanoresene	$(C_{14}H_{22}O)_n$	Tschirch and Halbey	62°	blood red	red	green, yellow	red, brownish green
Dracoresene	$C_{29}H_{44}O_2$	Tschirch and K. Dieterich	74°	dark red	red	dirty green, yellow	red, dark red, brown
α -Panaxresene	$C_{32}H_{54}O_4$	Tschirch and Baur	—	deep red	blood red	between yellow-brown and olive-green	brown-red, brown

Substances of totally different behaviour in the Hesse Reaction.

Isocholesterin	$C_{26}H_{44}O$	E. Schulze	137-138°	colourless, red later	pale yellow	—	red, yellow
Dammarresene	$\alpha : C_{31}H_{50}O$ $\beta : C_{31}H_{52}O$	Tschirch and Glimmann	65° 206°	red-yellow	pale yellow	indefinite	turbid rose red, then bluish
Chironol	$C_{28}H_{48}O$	Tschirch and Baur	173-176°	yellow, afterwards dirty violet	yellow, afterwards reddish yellow	faintly green	cherry red, violet

Substances imparting a slight Red coloration to Chloroform in Hesse's Test.

Abietic acid	$C_{19}H_{28}O_2$	Mauch	165°	reddish yellow	blood red	absence of characteristic transitions	red, violet, brown, green
Euphorbon	$C_{20}H_{36}O$	Henke	113–114°	reddish yellow	blood red	—	red, brownish green
Succinoabietol	$C_{40}H_{60}O_2$	Tschirch and Aweng	124°	reddish yellow	blood red	—	red, brown
Storesinol	$C_{16}H_{25}O_2$	Tschirch and van Itallie	—	reddish yellow	blood red	ill-defined	violet, bluish green, green
Myroxoresene	$C_7H_{10}O$	Tschirch and Germann	—	reddish yellow	brownish red	brownish	brown-red
α -Copalresene	$C_{14}H_{23}O_4$	Tschirch and Stephan	75–77°	reddish yellow	red	brownish yellow	brown
Benzoresinol	$C_{16}H_{26}O_2$	Tschirch and Lüdy	274° unc.	yellow, afterwards reddish yellow	blood red	ill-defined	cherry red, brown
Dammarolic acid	$C_{36}H_{80}O_8$	Tschirch and Glimmann	—	yellow, afterwards reddish yellow	red	—	red, dark red

Substances producing merely Yellow or no coloration with Chloroform in Hesse's Reaction.

Succinoabietic acid	$C_{80}H_{120}O_5$	Tschirch and Aweng	143°	yellow	red	ill-defined	reddish brown
Sandaracolic acid	$C_{45}H_{66}O_7$	Tschirch and Balzer	140 (152°)	yellow	red	—	reddish brown
Boswellic acid	$C_{32}H_{52}O_4$	Tschirch and Halbey	142–150°	yellow	blood red	—	red, dark brown-red
Chironolic acid	$C_{25}H_{48}O_4$	Tschirch and Baur	100–108°	yellow	red	—	red
Trachylolic acid	$C_{36}H_{88}O_8$	Tschirch and Stephan	165°	yellow	red	—	red-brown, dirty brown
Callitricolic acid	$C_{45}H_{84}O_8$	Tschirch and Balzer	248°	yellow	blood red	—	red, red-brown
Copalbic acid	$C_{30}H_{50}O_2$	H. Rose	—	yellow	red	—	red, red-brown
β -Panaxresene	$C_{32}H_{52}O_5$	Tschirch and Baur	—	yellow	blood red	—	red-brown
Isotrachylolic acid	$C_{36}H_{88}O_8$	Tschirch and Stephan	105–107°	yellow	dark red	brown-yellow	brown
β -Copalresene	$C_{35}H_{88}O_4$	Tschirch and Stephan	—	yellow	red-yellow	brown-yellow	brown

Substance.	Formula.	Analyst.	Melting-point.	Hesse's Reaction.		Drop Coloration in the Porcelain Basin.	Liebemann's Reaction.
				CHCl ₃	H ₂ SO ₄		
Guaiaconic acid	C ₂₀ H ₂₄ O ₅	Döbner and Lückner	95-100°	pale yellow	dark violet	yellow, blue-green, green	dark violet
Pinosresinol	C ₁₈ H ₁₈ O ₆	Bamberger	80-90°	colourless	red, red-violet	—	red, brown-red
Lanicesresinol	C ₁₆ H ₁₉ O ₅	Bamberger	161°	colourless	rose red	—	rose red
Myroxol	C ₄₆ H ₆₈ O ₁₀	Tschirch and Hermann	—	colourless	dark red	yellow	brown
Guaiac acid	C ₂₀ H ₂₄ O ₄	Döbner and Lückner	75-80°	colourless	rose red	—	rose red
Succinoresinol	C ₁₂ H ₂₀ O	Tschirch and Aweng	275°	pale yellow	reddish	—	dirty brown
Myroxocerin	C ₁₃ H ₂₀ O	Tschirch and Hermann	95°	yellow	yellow	yellowish	faintly reddish
Alban	C ₄₀ H ₆₄ O ₂	Tschirch and Oesterle	195° unc.	pale yellow	yellow	—	red, brown-red
Agaric acid	C ₁₆ H ₃₀ O ₅ + H ₂ O	Jahns	138-139°	colourless	yellow	—	yellow
Podocarpic acid	C ₁₇ H ₂₂ O ₃	Oudemans	187/8°	colourless	yellow	—	purple-red, yellow-green
Aleuritic acid	(C ₁₃ H ₂₆ O ₄) _n	Tschirch and Farnet	101.5°	colourless	slightly yellow	—	slightly yellow
Myroxofluorin	C ₄₂ H ₆₄ O ₁₀	Tschirch and Hermann	—	colourless	yellow green	bluish, colourless	pale yellow, dark yellow

Uses of Resins.—These substances are widely utilised for technical, medicinal, and pharmaceutical purposes. Colophony, elemi, dammar, mastic, copal, amber, sandarach, and other light-coloured resins are more particularly employed in the preparation of varnishes, though some of them, *e.g.* copal, dammar, and amber, have to undergo certain preparatory treatments, such as distillation, fusion, etc., in order to convert the hard and comparatively insoluble resins into soluble products. The copal varnishes are the most highly esteemed of any. Colophony and acaroid resins are used for sizing paper, and are also distilled for the production of gas and resin oil, colophony, in particular, being very largely employed for this purpose. For pharmaceutico-medicinal uses—preparation of plasters, ointments, etc.—the balsams, storax, turpentine, colophony, and gallipot are utilised; and copaiba and Peruvian balsam belong to the category of highly efficacious medicaments. The turpentine in particular are worked up into a large number of primary and secondary substances, and furnish oil of turpentine, colophony, various kinds of pitch, resin oils, *resina pini*, etc. The gummy substances left behind in the treatment of gum resins are largely used as agglutinants. Taken altogether, the employment of resinous substances has been exceedingly varied and extensive from time immemorial.

Identification of Resins; Qualitative and Colour Reactions.—At first, qualitative methods alone were employed in the analysis and identification of resins. The colour reactions, in particular, were very numerous, and some of these are still employed in the absence of better methods. So great was the complexity of these various reactions, and so conflicting the results obtained therewith, that it is a source of gratification that modern attempts at establishing quantitative methods have shown they can be dispensed with. The most

important colour reactions of a general character are those of Storch-Morawski, Ellram (vanillin-sulphuric acid), and above all, the cholesterin reactions already described as due to Tschirch and his pupils. Mauch's proposal to perform the colour reactions with the oils isolated by means of chloral hydrate must also be considered a progressive step. Numerous special colour reactions, etc., are due to Hirschsohn; and, just as in the case of fats and oils the fatty acids are now considered the fittest subjects for the colour reactions, so Tschirch, by determining the cholesterin reactions of the resinotannols and the resinols, and K. Dieterich, by employing the resin alcohols and resin acids as the basis of quantitative and qualitative analysis, have brought the examination of the resinous substances more into line with that of the fats and oils, and therefore into a more reliable path than hitherto.

As already mentioned, and will be shown later on, the future of resin analysis, just as in the case of the fats and oils, lies in the selection of quantitative methods in preference to qualitative and colour reactions.

Identification and General Reference to Quantitative Methods of Testing.—The quantitative analysis of resins is divided into two branches—(1) quantitative identification; and (2) actual quantitative investigation for purity. Although the identity of a resin can mostly be determined by the external and physical characteristics, and confirmed by its chemical behaviour and the above-mentioned qualitative reactions, there are also certain quantitative constants, such as the acid, ester, and saponification values, which afford information, not only as to whether the product is really the resin it is supposed to be, but also whether it is free from extraneous admixtures.

Melting-point, Specific Gravity, Ash, Moisture, Special Determinations.—Further quantitative estimations that may

be performed are : the conditions of solubility, melting-point, specific gravity, percentage of ash and moisture, and such special determinations as testing for cinnamein in Peruvian balsam, the carbonyl, methoxyl, acetyl values, and the investigation of the resin acids and resin alcohols.

Solvents.—The principal quantitative methods of testing for purity are not such as are applicable to merely subordinate constituents of the resins—*e.g.* the carbonyl value—but those referring to the main constituents. To this class belong the acid and saponification values, or the quantitative determination of the portions extractable by various solvents—alcohol, ether, etc., and, more recently, chloral hydrate (Mauch¹)—as formerly practised by Guichard, Hirschsohn, Kremel, E. Dieterich, etc., and continued by K. Dieterich.

An interesting precursor of chloral hydrate for this purpose was sodium salicylate, which, according to Conrady, is capable of partially or entirely dissolving numerous resins and gum resins. Flemming's method of dissolving copal and amber in epi- and di-chlorhydrin is also worthy of mention ; and the following table shows the results of Valenta's application of these solvents to a large number of resins :—

RESIN.	EPICHLORHYDRIN.	DICHLORHYDRIN.
Elemi.	Readily and completely soluble, both in the cold and the warm, forming yellow to greenish solutions, which leave a clear, sticky residual layer on evaporation.	Readily and completely soluble. The solution turns brown when warmed.
Mastic.	Readily soluble in the cold or warm. Solution pale yellow, leaving a lustrous, colourless layer on evaporation.	Less readily soluble. The solution turns brown when warmed.

¹ Dissertation, Strassburg, 1899.

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RESIN.	EPICHLORHYDRIN.	DICHLORHYDRIN.
Dammar.	Imperfectly soluble; more readily so in the warm. The clear yellowish filtrate gives a solid, clear, colourless layer of varnish.	Dissolves fairly readily to a brown solution in the cold. When warmed, the colour turns to deep brown-violet.
Courbaril Copal.	Imperfectly soluble in the cold, almost entirely so in the warm, to a clear yellowish varnish.	Perfectly soluble in the cold to a yellow solution, which turns brown when warmed.
Dragon's-blood.	Readily soluble, except for a brown residue. The solution is blood red, but gives a clear layer of varnish.	Imperfectly and less readily soluble; solution yellowish red in colour.
Sandarach.	Imperfectly soluble in the cold or warm. Solution pale yellow.	Dissolves perfectly in the cold to a brownish yellow solution, becoming deep brown when warmed.
Bleached Shellac.	Sparingly soluble; imperfectly so even in the warm.	Readily and perfectly soluble in the warm. Solution yellowish, does not turn brown; varnish layer dries very slowly.
Zanzibar Copal.	Partially soluble in the cold, more readily in the warm. Solution light yellow in colour, and gives a hard, clear stratum.	Partially soluble in the cold to a brownish solution, turning dark brown when heated.
Angola Copal.	Partially soluble in the cold, more readily in the warm. The faint yellow solution gives a solid varnish layer.	More readily soluble. Solution turns brown when warmed.
Manila Copal.	Partially soluble in the cold (the insoluble portion swelling up to a gelatinous mass), almost completely so in the warm. Gives a yellow solution, and solid varnish layer.	The greater part soluble in the cold. The brownish yellow solution turns brown when warmed.

RESIN.	EPICHLORHYDRIN.	DICHLORHYDRIN.
Kauri Copal.	Partially soluble in the cold (the remainder swelling up), perfectly so in the warm. Colour pale yellow; varnish clear.	Almost perfectly soluble to brownish yellow solution, which turns brown when warmed.
Amber.	Partially and very slowly soluble. Solution yellow.	Sparingly soluble. The lumps of amber turn brown when heated.
Asphaltum.	Very sparingly soluble, cold or warm.	Very sparingly soluble, cold or warm.

With regard to the solubility of resinous substances, it may be remarked that a certain amount of error may be introduced into the quantitative determination of the soluble portions by the absorption of oxygen in drying, special attention to which has been drawn by Weger's researches on oxygen absorption by resins. Furthermore, it should be remembered, in case of conflicting reports, that the age of the resin and the time it has lain on the ground or covered up in the soil (*e.g.* dammar and sandarach) exercise great influence on its solubility. When quite fresh, both dammar and sandarach, also recent fossil resins, are more readily soluble than after a long sojourn in the place of discovery. Thoroughly fossilised resins, like the true copals, are, in consequence of their age, either soluble with great difficulty or almost entirely insoluble.

Sack gives the following particulars with regard to the solubility of the resins. His reports, however, do not correspond in a more than approximate manner with present-day experience:—

Alcohol readily dissolves colophony, shellac, sandarach, and mastic, whereas elemi is only sparingly soluble, copal cakes

together, and dammar and amber are totally insoluble in this solvent.

Ether readily dissolves dammar, colophony, elemi, sandarach, and mastic; copal swells up; and amber and shellac remain undissolved.

Acetic acid has no action on any of the resinous substances except colophony, which swells up.

Caustic soda readily dissolves shellac, but colophony is only sparingly soluble, and the others not at all.

Carbon di-sulphide readily dissolves dammar and colophony; elemi, sandarach, and mastic with difficulty; copal swells up; and shellac and amber remain insoluble.

Oil of turpentine is a very good solvent of mastic, and a fair one of dammar, colophony, elemi, and sandarach, but does not dissolve shellac or amber, and merely causes copal to swell up.

Benzol dissolves dammar, colophony, and mastic very well, but is a poor solvent of elemi and sandarach, and does not dissolve amber or shellac.

Petroleum ether dissolves only dammar and mastic well, colophony, elemi, and sandarach badly, and the others not at all.

Boiling linseed oil has no solvent action on copal or amber, and dissolves shellac, elemi, and sandarach with difficulty, but readily takes up dammar, colophony, and mastic.

Ammonia dissolves none of the resins, but colophony, with ease.

Concentrated sulphuric acid dissolves all the resins to brown solutions, except dammar, which furnishes a bright red liquid.

The solubility of the resins in carbon di-sulphide formed the subject of special study by Guichard.¹

Acid Value.—This constant (for definition, see Introduction to Part II.), which is useful in the quantitative analysis

¹ *A. d. Ph.* 205, p. 537; 207, p. 565.

of resins, was at first determined by dissolving the resin or balsam in alcohol and titrating the solution with alkali direct, in a manner analogous to the Hübl method for fats; in the case of gum resins it was customary to make an alcoholic extract, generally, as stated in the Preface, in a very questionable manner. As, with very many resins, especially where alcoholic extracts were used, the high coloration of the liquid rendered the titration very inaccurate, attempts have recently been made by K. Dieterich to obtain, by back titration, a liquid better suited for the purpose in view. In this method the alkali serves at once to neutralise the acid, and acts as a solvent. Moreover, it presents the advantage, especially in the case of ester-free resins like copal, sandarach, dammar, etc., that all the resin acids are quantitatively combined. That this is not always the case with direct titration is shown by the results, which sometimes come out too low, and at other times are exceedingly variable.

Again, with a number of resins which, like olibanum and asafœtida, are difficult to saponify by the cold process, the acid value can be determined by back titration, although they contain esters. In such cases the mixture may be left for twenty-four hours without fear of saponification occurring, the esters present being very slow to saponify, at least in the cold. On the other hand, though with the various kinds of benzoin the acid value should be determined by back titration, the mixture should not be left for more than five minutes, or saponification may ensue. The great advantage of back titration with all these resins is that, unlike the direct method, no solution has to be prepared, and no extracts or dark coloured liquids difficult of titration are obtained, but fairly pale, alkaline solutions of resin, easy to titrate, and furnishing a clearer end reaction from red to white or yellow, than the change from brownish yellow to red given by the direct

method. Furthermore, Dieterich has elaborated a steam distillation process, analogous to the Reichert-Meissl method in fats, for driving off the volatile portions of such resins as are rich in ethereal oils and similar constituents (*e.g.* ammoniacum, galbanum, etc.). This method is, however, somewhat cumbrous, and requires considerable practice in its performance; but the author has also worked out a simpler process for ammoniacum and galbanum, consisting in the back titration of an aqueous alcoholic extract, so that the above determination of the volatile matters need not be performed except in doubtful cases. The main reason for employing back titration here is the one already given, namely, that the change from red to yellow on reaching the end-point is much sharper than that from yellowish brown to brown-red or red in direct titration. It may also be mentioned that the commercial grades of ammoniacum and galbanum have greatly deteriorated of late years, so that the values given by Dieterich as normal for the volatile matters in these substances can no longer be taken to apply to the ordinary commercial qualities, but must be lowered.

The acid-value determination of myrrh is performed in a somewhat different manner, back titration being impracticable owing to incipient saponification. Most of the gum resins, being only partially soluble in alkali, require to be extracted by boiling with water and alcohol (each a quarter of an hour in succession) under a reflux condenser.

Saponification Value.—In determining the saponification value, the hydrolysis was formerly effected as a rule by a longer or shorter boiling with stronger or weaker caustic potash,—after the manner of the Hübl method for fats. Sometimes an extract, at others the crude resin, was employed, the values in any event being subject to great fluctuation by reason of the lack of uniformity in the

performance of the method. Thus, Mills continued the saponification for eighteen hours in a closed flask; Williams boiled for half an hour under a reflux condenser; Kremel, von Schmidt, Erban, Beckurts, and Brüche followed the same plan, but for the most part employed extracts from the drugs examined; and E. Dieterich also pursued the same course, but generally concentrated the mixture until the alcohol was expelled, and then took up the residue again with water and alcohol. In consequence of this variability, K. Dieterich attempted an improvement consisting in employing for each kind of resin the special method of saponification found most suitable to the case. Thus a trial—yielding only negative results—was made with Tschirch's saponification method by passing hot steam through the alkaline liquid. Unfortunately none but very irregular decomposition values could be obtained, the method proving unsuitable for analytical purposes, though well adapted for saponification on a large scale. After further experiments, Dieterich succeeded in finding two saponification methods for the various resinous substances, on lines precluding decomposition values and ensuring perfect saponification, whilst furnishing liquids highly suitable for titration. These methods are the "cold" and "fractional" saponification tests.

Cold and Fractional Saponification.—Of these methods the first named has been more particularly tried on resins, whilst the fractional method is more suitable to the gum resins, the latter containing substances accessible to the action of alcoholic alkali on the one hand and aqueous alkali on the other. These methods have proved applicable to a number of resins, the main advantage being that perfect saponification can be secured with the natural drugs without the necessity of preparing extracts or

solutions of the whole or a portion beforehand. Whilst in the cold saponification method the resin is simply left exposed to the action of benzine (sp. gr. 0·700) for twenty-four hours at room temperature, the fractional method entails a preliminary saponification with alcoholic alkali alone. A second saponification follows, which, just as the first was left for twenty-four hours in contact with the alcoholic alkali, is continued for twenty-four hours with aqueous alkali. The higher final values show that the gummy constituents of the gum resins are not completely saponified before the final aqueous treatment.

Resin Value; Total Saponification Value; Gum Value.—The term “resin value” is applied by the author to the result of the simple alcoholic saponification + benzine, the result of the method employing alcoholic + aqueous alkali + benzine being named “total saponification value,” whilst the difference between the two is the “gum value.” (An explanation of these terms is given in the Introduction to Part II., p. 57.)

Since the saponification proceeds in definite sections, and certain constituents of the resins and gum resins are saponified separately, the name “fractional saponification” is regarded as *à propos*. Certain resins, etc., which do not lend themselves to either of these cold processes, have still to be saponified by the hot method, under a reflux cooler and according to definite conditions. Special reference will be made at the conclusion of this section to the resins that can be saponified without recourse to heat. For such of the resinous products as have not yet been allotted any special method of saponification, the sole plan that can be accepted as uniform and suitable is that of saponification for half an hour under a reflux condenser, and back titration after cooling, *i.e.* the method adopted by Hübl for fats.

Ester, Ether, and Anhydride Values —When the acid and saponification values are determined in separate experiments, the ester and ether values are found by subtracting the acid value from the saponification value. Where the ester value is ascertained in the same experiment as, and subsequent to, the acid value, by neutralisation followed by a further addition of alkali and saponification by one of the aforesaid methods, the saponification value is obtained indirectly, by adding together the acid and ester values. The term “ester value” is used in all, or at least in the principal, works on the subject (such as those of Kremel, Williams, Beckurts and Brüche, E. Dieterich, K. Dieterich, etc.), and not “ether value.” Consequently the former term is correct for these values and for the esteriferous resins, even though synonymous with “ether value” and obtained by the same means. The “anhydride value” which expresses the amounts of true inner anhydrides, lactones, ester-anhydrides, and alcohol-anhydrides is not—as proposed by Benedikt—to be confounded with the ether and ester values. Benedikt also—in a manner decidedly open to objection—altered to “ether values” the values previously designated “ester values” by Kremel, von Schmidt, and Erban. The author prefers to style all these values “ester values,” since the true ethers, which would justify the term “ether value,” have so far not been found in any of the resins but colophony.

Constant Ether Value.—In the case of colophony which was first shown by K. Dieterich to be devoid of esters, but which, according to Henriques, contains ethers and lactones, it has been proposed by the last-named worker to apply the term “constant ether value” to the values referring to these constituents. In any event the term “ether value” is more applicable to colophony than

“ester value” would be, in the absence of any esters at all in that substance; and, moreover, as at present esters alone are known to exist in all other resins, it follows that the term “ester value” should be confined to resins containing esters. It should be mentioned that the ester and saponification values of resins often express other and secondary reactions, not merely the phenomenon of hydrolysis alone, and that these constants must be regarded more as empirical than as theoretical and scientifically accurate values.

For the further characterisation of the resins numerous methods have latterly been proposed, most of which are tedious and based on subsidiary constituents of the resins, nor have they sufficient practical importance to entitle them to mention, except as a matter of theoretical interest. These comprise the acetyl (HO group) value method for resins (K. Dieterich), the carbonyl value method (CO and COH groups) by Kitt, the methoxyl value method (OCH₃ groups) by Gregor, and the examination of the resin acids and resin alcohols by K. Dieterich. (The definition of these different values will be found in the Introduction to Part II.)

Acetyl Value ; Carbonyl Value ; Methoxyl Value.—In the method proposed by K. Dieterich¹ for determining the *acetyl value* of resins, the substance is boiled under a reflux condenser, with an excess of acetic anhydride and a little anhydrous sodium acetate, until completely dissolved, or until it is evident that no further portion will pass into solution. The solution is poured into water, and the precipitate then ensuing is collected and extracted with boiling water until perfectly free from all traces of uncombined acetic acid. The insoluble residues left by copal and dammar are also treated in the same manner. The dried acetylated products are then tested for the acetyl, acid, ester, and

¹ *H. A.*, 1897, pp. 39–45.

saponification values by dissolving 1 grm. in cold alcohol and titrating with $\frac{1}{2}$ normal caustic potash. The saponification is also effected with $\frac{1}{2}$ -n alkali for half an hour under a reflux condenser, and the product titrated back after cooling down and dilution with alcohol (not water). As in the case of fats, the difference between the acetyl-saponification value and the acetyl-acid value gives the true "acetyl value."

Kitt's "**Carbonyl Value**":¹—The substance under examination is warmed with sodium acetate and an accurately measured quantity of phenylhydrazine chloride in dilute alcoholic solution. The excess of hydrazine salt not sharing in the reaction is then ascertained by eliminating the nitrogen by oxidation with Fehling's solution and collecting the gas in a measuring tube. The carbonyl value, *i.e.* the percentage of carbonyl oxygen in the substance taken, is ascertained by the formula $O = V - V_0 \frac{0.07178}{S}$, wherein $V - V_0$ indicates the difference in the volume of nitrogen reduced to 0 or 760 mm., and S refers to the weight of the substance in grms.

The Gregor-Bamberger "**Methoxyl value**" (Zeisel):²—As this method entails the use of apparatus and special precautions, it is considered preferable to repeat the author's own description in full.

The Zeisel apparatus is made up as follows:—A reflux condenser, fed with water at 40°–50°C., is fitted with a small flask, the neck of which is provided with a lateral tube for the introduction of carbon dioxide. The upper end of the condenser tube is connected with a Geissler potash apparatus which is charged with amorphous phosphorus suspended in water, and is placed in a water bath kept at about 50°–60°C., its purpose being to free the current of alkyl-iodide vapour passing through from hydriodic acid and iodine vapour.

¹ *Ch. Ztg.*, 1898, p. 358.

² *Oest. Ch. Ztg.*, 1898, Nos. 8 and 9.

The alkyl iodide is led into a 4 per cent. solution of silver nitrate in two successive flasks, the whole being generally retained and converted into silver iodide in the first one. In performing the experiment, the substance to be examined for methoxyl is heated along with 10c.c. of hydriodic acid of sp. gr. 1.68, CO_2 being passed through the apparatus. The experiment is complete when the liquid in the first flask has become clear above the deposit of silver iodide, and the silver iodide is then determined by gravimetric means.

Since the publication of this method by Zeisel, the improvements made have been insignificant; Herzig¹ proposed to add acetic anhydride to the hydriodic acid used, whilst Benedikt and Gruessner simplified the apparatus.

Certain modifications were recently proposed by myself² for simplifying and quickening the method without impairing its accuracy, and which at the same time presented special advantages for technical investigations. They consist mainly in replacing the tedious gravimetric estimation of silver iodide by the equally precise and quicker method of Volhard, the alcoholic normal silver solution being acidified with nitric acid in order to hasten the decomposition of the alkyl iodide.

In charging the Geissler apparatus the use of amorphous phosphorus suspended in water is replaced by a solution of equal parts of potassium carbonate and arsenious acid in 10 parts of water, thus avoiding the reduction of the silver nitrate, in the tube dipping into the first flask, by the amorphous phosphorus. The arsenious acid fixes any stray iodine, being itself oxidised to arsenic acid, whilst the excess of potassium carbonate fixes the hydriodic acid, liberating merely the innocuous gas CO_2 .

Another advantage in the use of arsenious acid was

¹ *Monatshefte für Chemie*, 1888, ix.

² *Monatshefte für Chemie*, 1895, xix.

discovered in the course of the work, viz. when a substance containing sulphur is subjected to the methoxyl test, and amorphous phosphorus suspended in water is used, the liberated sulphuretted hydrogen, which of course cannot be retained in the Geissler apparatus, precipitates silver sulphide from the silver nitrate solution.

This was already known to Zeisel,¹ who therefore abstained from applying the method to bodies containing sulphur.

In making methoxyl determinations with sulphurous resins I observed a separation of arsenic sulphide in the Geissler apparatus charged with arsenious acid solution, but the silver nitrate in the receiver was free from traces of silver sulphide. It is necessary in such cases to keep the arsenious acid solution more dilute than usual, otherwise a copious deposition of arsenic sulphide may choke up the tubes of the Geissler apparatus.

To simplify the calculation when Volhard's titrimetric method is used, I employ a $\frac{n}{10}$ solution of silver nitrate, dissolving 17 grms. of pure crystalised AgNO_3 in 30 c.c. of water, and making the solution up to 1 litre with commercial absolute alcohol. This solution is standardised on $\frac{n}{10}$ potassium thiocyanate, which in turn is titrated with aqueous $\frac{n}{10}$ silver nitrate. The standard of the alcoholic solution undergoes some change on keeping, and must therefore be tested again.

For ordinary analyses it is sufficient to use 50 c.c. of the silver nitrate solution in the first flask, and 25 c.c. in the second, after acidification with a few drops of nitric acid free from nitrous acid. After the reaction is terminated—Zeisel's conditions being otherwise maintained throughout—the clear liquid above the silver iodide is poured off

¹ *Monatshefte für Chemie*, 1886, vii.

into a 250 c.c. measuring flask. The silver nitrate solution in the second flask is diluted with water and poured into the same measuring flask, the contents of which are thereupon made up to the mark with water, agitated well, and passed through a folded filter into a dry vessel.

For the titration, 50 or 100 c.c. of the filtrate are used, after suitable acidification with nitric acid (free from nitrous acid) and an addition of ferric sulphate solution.

The following example may serve as typical of the method:—

1·2064 grm. of Peruvian balsam was employed. Of the filtrate from the receiver—containing 75 c.c. $\frac{n}{10}$ silver nitrate solution made up to 250 c.c.—50 c.c. consumed 11·5 c.c. of $\frac{n}{10}$ potassium thiocyanate; consequently the total amount would consume $11·5 \times 5 = 57·5$ c.c. $\frac{n}{10}$ potassium thiocyanate, whilst the remaining 17·5 c.c. of $\frac{n}{10}$ silver nitrate was consumed in the production of silver iodide.

Now in order to determine the methoxyl value, it is merely necessary to multiply by 0·0015 the number of c.c. of $\frac{n}{10}$ silver nitrate consumed, since 1 c.c. of $\frac{n}{10}$ silver solution is the equivalent of 0·0015 grm. of methoxyl. Hence in this case the methoxyl value is $0·0015 \times 17·5 = 0·2625$, or, calculated to 1 grm. of Peruvian balsam, 0·0217, *i.e.* 21·7.

By using the Volhard titration the entire operation is complete within two hours, whereas with the Zeisel gravimetric method the work takes much longer. The values obtained by the two methods are very concordant, as evidenced in the examples published (*l.c.*), and I, therefore, prefer the “titrimetric method.”

The present is not a suitable occasion for discussing the value of these new methods, and all that need be said is contained in the following résumé of the author's paper (*Chem. Rev.*, 1899, No. 10):—

“In summing up, it may be stated that the newer methods of determining the acetyl value (K. Dieterich), carbonyl value (Kitt), methoxyl value (Gregor-Bamberger), may be welcomed as quantitative methods for characterising resins—provided they are properly applied to the appropriate resins—and also as supplementing the known methods of identification; but, owing to their limited applicability and tedious character, are by no means capable of replacing, far less superseding, the existing simple methods for determining the acid, ester, saponification, and other values which have proved so useful for identification and the detection of adulteration.”

Resin Acids ; Resin Alcohols and their Characteristic Values.—The author has repeatedly recommended the employment of the isolated resin acids and alcohols in connection with the analysis of resins. Naturally it would be necessary to accumulate further data, which are at present scanty, on such points as the difference between the resins and the pure resin acids—in ester-free resins—or the resin alcohols in resins containing esters. In this connection compare the reactions, already given, of the resinotannols, and the cholesterin reactions of the constituents of resins.

Separation of Resin Acids and Fatty Acids.—Gladding and Twitchell examined mixtures of fatty acids and resin acids, and recommended the following method for their separation :—

In the case of a fatty acid adulterated with resin, about 0.6 gm. of the substance is dissolved in 20 c.c. of 95 per cent. alcohol. To this solution is added a trace of phenolphthalein, and a solution of alcoholic potash is run in, drop by drop, from a burette, with continued stirring, until the indicator has assumed a dark red colour, characteristic of alkalinity.

After adding one or two drops of the potash solution in excess, the flask containing the liquid is placed on the water bath and the contents boiled for ten minutes. When cold, the whole is poured into a 100 c.c. test tube, the flask washed with ether, and—the whole being made up to 100 c.c. with this solvent—the tube is corked and shaken up thoroughly.

Next, 1 gram. of finely divided silver nitrate is introduced and shaken up well for ten to fifteen minutes, until the flocculent deposit of silver stearate or oleate has collected together at the bottom of the tube. Then 50–70 c.c. of the clear liquid are removed by means of a pipette, and transferred to another 100 c.c. test tube, where a further small quantity of silver nitrate is added to remove the fatty acid still in solution. The clear liquid is then mixed with 20 c.c. of dilute hydrochloric acid (one-third 21 per cent. HCl. and two-thirds water); an aliquot part of the supernatant ethereal solution is evaporated in a platinum basin, the residue—dried in the steamer—being resin, accompanied by a little oleic acid. Direct experiment has shown that, under these conditions, 10 c.c. of ether retain on an average 0.00235 gram. of oleic acid, so that the results of the analysis may be corrected by means of this coefficient. The method is applicable to the determination of resin in linseed oil, soap, etc.

This method has been tried and modified by Ulzer and Defris,¹ who published the results they obtained in the quantitative estimation of fatty acids in presence of the resin acids of shellac and pine resin. They found a considerable difference in the behaviour of these two classes of resin acids. A dark sample of shellac furnished, by the Gladding method, only 13.76 per cent. of resin acids, the silver salts

¹ *Zeits. f. Analyt. Chem.*, 1897, p. 27.

of which were for the most part insoluble in ether, whereas those from pine resin acids are soluble. When applied to the analysis of a mixture of 51 per cent. colophony and 49 per cent. shellac acids, the above separation method gave 48.46 per cent. of resin acids; but the concordance here experienced must be ascribed to a compensation of the sources of error, the colophony containing 12.9 per cent. of unsaponifiable constituents, and the shellac, 13.76 of acids resembling resin in character. A technical sample of varnish, composed of colophony and shellac, gave, after the expulsion of the alcohol, an iodine value 80.87, an acid value 111.30, and the saponification value 190.40, from which data the composition deduced was: colophony, 69.2 per cent., and shellac, 30.8 per cent. The separation method gave 63.7 per cent. of resin acids. From the above acid value, the composition would be expressed by: colophony, 59.3 per cent., and shellac, 40.7 per cent. Finally, the behaviour of the shellac acids in presence of the Twitchell method was examined, the result showing that, as in the case of fatty acids, the shellac resin acids form esters under the influence of a current of hydrochloric acid gas.

Copal resin acids were also examined by the Gladding and Twitchell method. It was found that the Gladding method could not furnish quantitative results, the reason for this being that a portion of the sodium soaps is separated from the alcoholic solution during neutralisation, the precipitation being increased by the subsequent addition of ether. The Twitchell method gave 81.01 per cent. of resin acids from Angola copal, and 86.37 per cent. from Cowrie copal.

Although belonging rather to the domain of fat analysis, the above method is referred to here because it is based on the properties of different resin acids, and because

mixtures of resins and fats are largely used for technical purposes, and the chemist has frequently to undertake the separation of resin acids from fatty acids in resin analysis, just as the converse separation has to be effected in fat analysis. As Weger very rightly pointed out in his researches on oxygen absorption by resins, the above method cannot give more than relatively correct values, since, in the course of drying, the resin acids are subjected to the oxidising influences described by Weger, which affect the results to a considerable extent.

Iodine and Bromine Values.—We have already seen that, in a chemical sense, the relationship between fats and resins is, so to speak, *nil*, but that, nevertheless, the methods employed for the examination of the former bodies can also be successfully applied to the latter. Less satisfactory, however, are the iodine values and the bromine values determined by Iliney, Mills, and Muter; but, according to K. Dieterich, these are of subordinate importance for the resins—as other authors have also shown, in special instances—the conclusions drawn from the iodine value being very liable to error, apart from the inaccuracy caused, in the determination of this value, by the dark colour of the liquid for titration and by the use of extracts instead of the natural drugs. Consequently the bromine and iodine values are merely mentioned here, and are altogether omitted from the special part, for the reasons aforesaid.

Suitable Quantitative Methods.—The following quantitative methods are in use for, and are applicable to, the estimation of balsams, resins, and gum resins:—

- a.* Acid value, by various methods.
- b.* Ester value, direct or indirect.
- c.* Saponification value, or resin value and gum value, by various methods.

- d. Percentage of moisture.
- e. Ash.
- f. Percentage soluble in alcohol.
- g. Percentage insoluble in alcohol.
- h. Specific gravity.
- i. Percentage soluble in other solvents.

Further:

- k. Special determinations, such as cinnamein and resin esters in Peruvian balsam.
- l. Identity reactions, partly coinciding with *a*, *b*, and *c*.
- m. Acetyl, carbonyl, and methoxyl values.
- n. Examination of the resin acids and resin alcohols.
- o. Qualitative reactions.

According to the nature of the substance under examination the following methods of determining the important acid and saponification values are available.

Systematic Résumé of the Performance of the Acid and Saponification Value Tests.

A. ACID VALUE.

1. By direct titration (S.-Z. d.)¹:

- (a) Of the complete solution of the soluble resinous matter in alcohol, chloroform, etc.

Performance.—1 grm. of the substance is dissolved in a suitable solvent or mixture, and is titrated with alcoholic $\frac{n}{2}$ or $\frac{n}{10}$ caustic potash in presence of phenolphthalein, until a red coloration is produced.

Examples.—Nearly all such resins as are soluble, and for which no special method has yet been prepared.

¹ For the definition of these abbreviations, see Preface, and Introduction to Part II.

- (β) After the preparation of an alcoholic extract, in the case of imperfectly soluble resins, the said extract being employed for titration.

Performance.—Exactly similar to α , except that the result is calculated to 1 gm. of the extract instead of 1 gm. of the crude product.

Examples.—Gum resins, benzoin, storax.

- (γ) Of the solution obtained by extracting a partially soluble resin with alcohol and water.

Performance.—One gm. of the finely ground resin is extracted by boiling with 30 c.c. of water under a reflux condenser for fifteen minutes, followed by an addition of 50 c.c. of 96 per cent. alcohol, and re-boiling for an equal period. After cooling, the extract is titrated, without filtration, with $\frac{n}{2}$ alcoholic caustic potash and phenolphthalein, until a red coloration appears.

Examples.—Myrrh, bdellium, opopanax, and sagapenum.

2. By back titration (S.-Z. ind.):

- (α) In the case of entirely (or nearly) soluble resins, free from esters, where the alkali combines with the acid, and at the same time dissolves the whole of the resin.

Method.—One gm. of the finely divided (ester-free) resin is left in contact with 25 c.c. of $\frac{n}{2}$ alcoholic potash and 50 c.c. of benzine in a stoppered flask for twenty-four hours—or until solution has been carried as far as possible—and is then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

Examples.—Dammar, sandarach, mastic, guaiacum, copal, etc.

- (β) In the case of partially soluble—esteriferous, but sparingly saponifiable—resins, where the alkali fixes the acid and extracts the acid constituents.

Method.—One gram. of the finely powdered substance is left for twenty-four hours in contact with 10 c.c. of alcoholic $\frac{n}{2}$ potash and 10 c.c. of aqueous $\frac{n}{2}$ potash in a stoppered flask; it is then mixed with 500 c.c. of water and titrated back.

Examples.—Asafoetida, olibanum.

- (γ) Resins that are only partially soluble and contain esters, an aqueous alcoholic extract being employed.

Method.—One gram. of the finely divided resin is boiled for fifteen minutes under a reflux condenser with 50 c.c. of water, after which 100 c.c. of strong alcohol are added and the whole is boiled up again for another fifteen minutes. After cooling, the liquid and substance are made up to 150 grms. and filtered, 75 c.c. of the filtrate (= 0.5 gram. of substance) being treated for exactly five minutes with 100 c.c. of alcoholic $\frac{n}{2}$ potash, and then titrated back with $\frac{n}{2}$ sulphuric acid.

Examples.—Ammoniacum, galbanum, gamboge.

- (δ) In the case of resins which contain esters, are almost entirely soluble, and saponify readily: the natural drugs are used.

Method.—Ten c.c. of $\frac{n}{2}$ alcoholic potash are left to act for five minutes on the finely divided natural drug, and the solution is then titrated back.

Example.—Benzoin.

3. *By estimating the volatile acids* (in the case of gum resins rich in ethereal oils) (S.-Z. f.).

Method.—One-half gram. of the substance is suffused with a little water in a flask, and a current

of steam is passed through, the flask being placed on a sand bath to prevent excessive condensation. The receiver is charged with 40 c.c. of aqueous $\frac{n}{2}$ potash, into which dips the tube from the condenser. Exactly 500 c.c. of distillate are collected, the condenser tube is swilled out well with distilled water, and the whole is titrated back in presence of phenolphthalein. In this case the acid value gives the number of mgrms. of KHO neutralised by 500 c.c. of distillate from 0.5 gm. of resin.

Examples.—Ammoniacum, galbanum.

B. ESTER VALUE (E.-Z.).—This is always ascertained indirectly by calculation, *i.e.* subtracting the acid value from the saponification value, except in cases where the acid value has been determined as under *A. 3*, and where a resin value and total saponification value are present. In such event the ester value cannot be calculated.

C. SAPONIFICATION VALUE.

1. By the hot method (V.-Z. h.):

(*a*) In the solutions of completely soluble resins.

Method.—One gm. of the resin is dissolved and kept on the boil for half an hour in a steam bath, with 25 c.c. of alcoholic $\frac{n}{2}$ potash, under a reflux condenser. After dilution with alcohol, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

Examples.—Nearly all balsam sand resins for which no special methods have been devised.

(*β*) With a previously prepared alcoholic extract of a partially or sparingly soluble resin.

Method.—The same procedure exactly as under *a*, except that an alcoholic solution of the extract

is taken, the results being calculated to 1 grm. of the crude drug, and not of the extract.

Examples.—Gum resins, benzoin, storax.

- (γ) As *a*, except that the crude drug is taken after an addition of water to dissolve out the gummy matter.

Example.—Myrrh.

2. Cold method (V.-Z. k.):

- (*a*) For perfectly soluble resins, with cold alcoholic alkali and benzine only.

Method.—One grm. of the substance is treated in a stoppered 500 c.c. glass flask with 50 c.c. of benzine (sp. gr. 0.700 at 15° C.) and 50 c.c. of alcoholic $\frac{n}{2}$ potash. After standing for twenty-four hours at room temperature, it is titrated back with $\frac{n}{2}$ sulphuric acid; in the case of Peruvian balsam, for instance, about 300 c.c. of water must be added to dissolve the precipitated salts.

Examples.—Peruvian balsam, copaiba balsam, benzoin, storax.

- (β) Fractional saponification, including “resin value” and “gum value,” in the case of imperfectly soluble resins—alcoholic and aqueous alkali, with an addition of benzine to each, being used in succession.

Method.—Two samples, each of 1 grm., of the resin are powdered and suffused in separate 1 litre stoppered flasks with 50 c.c. of benzine (sp. gr. 0.700 at 15° C.), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash. After standing (closed) for twenty-four hours at room temperature, with frequent shaking, the one sample is shaken up with 500 c.c. of water and titrated back with

$\frac{n}{2}$ sulphuric acid and phenolphthalein; this gives the resin value (H.-Z.). The second sample is then treated further with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and is left for another twenty-four hours, with frequent shaking, being finally diluted with 500 c.c. of water and titrated back as above. This gives the "total saponification value" (G.-V.-Z.), the difference between this and the resin value being the "gum value" (G.-Z.).

Examples.—Ammoniacum, galbanum, gamboge.

By reason of the analytical labours of Kremel—who was the first to systematically transfer to resins the quantitative methods employed on fats, though he was closely followed by von Schmidt, Erban, Mills, Williams, Beckurts and Brüche, E. Dieterich, etc.—and others, a large collection of experimental material has been accumulated. From these a number of general and particular axioms have been deduced by K. Dieterich, who has also employed as a basis the results of his own investigations into Peruvian balsam, Copaiba (Angostura, Bahia, Carthagen, Illurin, Para, Maracaibo, Surinam, Gurjun) balsam, Mecca balsam, Benzoin (Siam, Sumatra, Padang, Palembang, Penang), Colophony, Copal, Dammar, Elemi, Palm dragon's-blood, Socotra dragon's-blood, Guaiacum, Mastic, Sandarach, Storax, Thapsia resin, Anime, Caranna resin, Ladanum Turpethum resin, Ammoniacum, Asa-foetida, Galbanum, Myrrh, Bdellium, Opopanax, Sagapenum, and Olibanum. These axioms are now given with the corresponding examples for those of a special character:—

General Axioms.—Generally speaking, the great fluctuations hitherto noticed in the analytical values obtained with resins—apart from the divergences *à priori* due to the variable composition of the resins themselves—are attributable to the following considerations:—

1. The lack of uniform, rational methods, with well-defined conditions of performance.
2. The scant individualisation of the current methods, and disregard of the modern chemistry of the resins.
3. The use of extracts in place of the natural drugs.
4. The lack of tests performed on authentically pure resins, taken direct from the parent tree, as a basis for the determination of value. (Up to the present time only a few authentically pure resinous bodies, such as Peruvian balsam, storax, and a few more, have been examined.)

According to K. Dieterich the following points should be considered in attempts to improve resin analysis:—

1. The use of the natural drugs instead of extracts.
2. The prescription of uniform conditions in the performance of rational methods.
3. Individualising these methods on the basis of modern resin chemistry.
4. Employment of quantitative methods in preference to qualitative methods—especially colour reactions.
5. Fixing normal limits for constant values, on the basis of the examination of authentically pure samples taken direct from the parent tree.

The following “special” points should be borne in mind in resin analysis:—

Special Axioms with Examples.—I. In any circumstance it is erroneous to employ only a portion—*e.g.* an alcoholic extract—of a resin or gum resin for analysis. When this is done, there occur—as has been shown in the case of Siam and Sumatra benzoin, storax, myrrh, ammoniacum, galbanum, etc.—losses and alterations which influence the results and preclude the formation of an accurate opinion on the natural drugs themselves. On this account the greater

portion of the resin values recorded in the literature of the subject, having been obtained in this imperfect manner, are restricted to a merely relative utility. The values obtained by using an extract cannot therefore in any case be regarded as applicable to the crude product.

II. Still less acceptable are values obtained by using 1 grm. of extract instead of the amount of extract corresponding to 1 grm. of crude drug, since 1 grm. of extract refers to much more than 1 grm. of crude drug, and therefore furnishes values in no way approximating to the definition "acid value" or "ester value."

III. Where possible, the previous preparation of a hot alcoholic solution without employing a reflux condenser, etc., should be avoided, as causing a loss of volatile matters, especially in the case of substances that are sparingly or only partially soluble (*e.g.* gum resins, storax, etc.).

IV. All methods employing back titration are practical, because they utilise the alkali both for fixing the acid and, at the same time, for acting as a solvent, and give a better end reaction (red into yellow) than the ordinary direct titration methods (for ammoniacum, galbanum, asafoetida, benzoin, olibanum, etc.).

V. With some resins (mostly free from esters) it has been found that, although soluble in inert solvents, the acid is not quantitatively and promptly fixed in direct titration methods; consequently they must be treated by the back titration method, and time must be given for the fixing of the resin acids. (To these resins belong: guaiacum, copal, dammar, sandarach, mastic, etc.) In this case also the end reaction is very well defined (colour-change red to yellow).

VI. Again, in the case of such ester-free or sparingly saponifiable resins as can be titrated direct with but slight variation, the back titration method is preferable for deter-

mining the acid value, because no preliminary solution is required, the alkali itself serving as a solvent, and giving a sharper end reaction from red to yellow than is possible with the converse change. The values obtained are generally more concordant than those from the direct method.

VII. Earlier saponification tests were frequently attended with the drawbacks that the values furnished were merely imperfect, or the dark-coloured liquids produced were difficult to titrate, contained decomposition products, or furnished merely relatively usable values because of the use of extracts in place of the natural drugs (*e.g.* Peruvian balsam, Siam benzoin, Sumatra benzoin, etc.).

VIII. Provided the natural drugs be used, the best results are furnished by the cold and fractional saponification methods, mainly because the liquids obtained are lighter in colour and more readily titrated.

It has been found that many resins can be saponified in the cold by alcoholic alkali and benzine, and many by the conjoined action of aqueous and alcoholic alkali in the cold. The first type of method is known as "cold saponification," the other as "fractional saponification"; in the latter the value given by the alcoholic alkali and benzine is termed the "resin value," and the result furnished by the aqueous and alcoholic alkali is the "total saponification value."

Furthermore, it has been found that nearly all the balsams, and many resins, can be completely saponified in twenty-four to forty-eight hours, without heat, by the simple cold method; and several of the gum resins and other bodies containing gum in addition to resin (except myrrh, olibanum, and asafoetida) can be effectually dealt with by the fractional method in the same time. However, with some gum resins it appears that only the fixation of the acid is affected by this means, without any saponification being produced.

The following are saponifiable in twenty-four to forty-eight hours by the cold process :—

Peruvian balsam.

Copaiba balsam	{ (Angostura, Bahia, Carthagena, Maracaibo, Maturin (East Indian), Para (West Indian) balsams)	} By alcoholic alkali and benzine.
Benzoin	{ (Siam, Sumatra, Palembang, Padang, Penang)	
Myrrh		
Storax		
Mecca balsam		} By fractional saponification.
Ammoniacum		
Galbanum		
Euphorbium		
Gamboge		
Dragon's-blood (Socotra, Sumatra)		
Lactucarium		

On the other hand, the following cannot be saponified by either method within the time specified :—

Asafoetida	} The use of alcoholic and aqueous alkali merely fixes the acids.
Olibanum	

It should be noted that the benzine should on no account be omitted, although for the most part it dissolves imperfectly.

IX. For the prevention of error, the acid and saponification values should be determined in two separate experiments.

X. In order to obtain solutions as free from colour as possible, only 1 gm. of any balsam, resin, or gum resin should be taken, instead of 3 grms. as in the case of fats. The increased margin of error in titration is not so great as the errors arising in the titration of darker liquids. Moreover, experiment has shown that the values obtained from 1 gm. are perfectly concordant with those furnished by 3 grms., and, in fact, greater concordance is found in the case of 1 gm. samples of pale resins.

XI. Dilution, whether of a solution or a saponification liquid, should rarely be practised with water, alcohol being generally necessary: the methods prescribed in each case should be carefully followed. Water usually produces milky turbidity, and gives a liquid difficult to titrate; or decomposition of the resin soap may ensue, as is the case with colophony, dammar, copal, etc. For this reason the use of, as far as possible, "water-free" plaster is advisable.

XII. The end reaction being quicker and better defined when $\frac{n}{2}$ alkali is used than with $\frac{n}{10}$ alkali, and the puzzling intermediate colour-changes being absent, it is always better to use the stronger alkali, despite the inherent errors in titration attending thereon.

XIII. Since the natural drugs, and not portions thereof, should always be used, it is very necessary to secure a good average sample, which is best obtained by grinding at least 100 grms. of the dry drug as finely as possible (see XXIII.). Balsams should always be well shaken up beforehand; resins containing water, *e.g.* storax, should be freed from moisture and stirred up well together. Gum resins, which are very soft and difficult to pulverise, are cooled by immersion in a refrigerant if necessary, and pulverised repeatedly until a good average sample is prepared, warmth being avoided in any event. When the parcel is large—entire boxes of benzoin, casks of storax, or bales of gum resin—the samples should be drawn from various parts of the bulk and not merely from one place. If, as is the case with myrrh, ammoniacum, galbanum, opopanax, and sagapenum, the gum resins are used direct, it is essential that the substance should be dissociated by boiling successively with alcohol and water, under a reflux condenser, especially before determining the acid value (whatever the method employed).

XIV. Naturally a single analysis is never sufficient to

afford grounds for an opinion in the examination of resins, duplicate determinations being essential, and the mean of the results must be taken. For cold saponifications, especially when the liquids must be left to stand a long time, stoppered glass flasks, holding 1 litre, should alone be used. Resins or balsams that are difficult to weigh out should be weighed on a glass rod, which is then placed, along with the substance, in the saponification liquid or glass flask.

XV. All results should be calculated to the natural crude drug, and not, as is frequently done, to the goods dried at 100°C . At least, both values should be given together.

XVI. The determination of the iodine and bromine values is of little importance, being in the first place a frequent source of error, and also furnishing inaccurate values by reason of the difficulty in detecting the end-point. (The iodine values of nearly all the resins and balsams have been determined—in the former case from the alcoholic extracts.)

XVII. Resins containing acids and esters can furnish acid and saponification values, whereas such as contain merely esters or free resin acids, can only yield the corresponding saponification or acid value, as the case may be.

Thus it is impossible to speak of the "acid value" of dragon's-blood, this body containing no free acids; or of the "ester values" of ester-free resins like colophony, sandarach, copal, dammar, etc. Values of this kind recorded in the literature of the subject are useless, and should be eliminated.

XVIII. Quantitative methods are all preferable to those of a qualitative character, the best of all being such as relate not merely to subordinate constituents of the resins, present in small amount therein, but such as are concerned with the principal components. In addition, no methods can claim to have any real worth except they have been found

reliable when systematically applied to adulterated resins as well as the pure substances.

XIX. As with fats, the acetyl value furnishes some guidance in forming an opinion, the more so, because nearly all the resins contain oxyacids.

Thus, the acetyl products of the turpentine vary considerably from one another and from the initial product. Similar conditions prevail in dammar, copal, etc. (see *Helfenberger Annalen*, 1897, pp. 39–44). Of the carbonyl and methoxyl values, as well as the resin alcohols and acids, mention has already been made.

XX. Generally speaking, the methods used in the examination of fats and oils are also applicable to the balsams, resins, and gum resins, though it should be borne in mind that the resins—being mixtures that have probably sustained considerable alteration in collection and by external influences, and not always homogeneous substances—cannot be investigated by any single method applied to the whole, but that it is necessary to fit the methods to the special resin, balsam, or gum resin under examination. Even a slight deviation from the lines already laid down with precision will bring about changes in the results.

XXI. Phenolphthalein has proved the best indicator for the, oftentimes strongly coloured, titration liquids. Other indicators, such as tropæolin hæmatoxylin, litmus, rosolic acid, methyl orange, and alkali blue, have all had to be discarded as more or less useless.

XXII. The alcoholic potash solution used for the cold and fractional saponification tests should be as rich as possible in alcohol, *i.e.* 96 per cent. spirit is used, and the liquid is filtered off from the insoluble K_2CO_3 .

XXIII. In comminuting and reducing to powder the resins (see VIII.), gum resins, and all products that are

sticky when rubbed together, prolonged heating in a drying oven, or even a preliminary warming, must be avoided on account of the aromatic constituents, and the end in view must be attained by storing the substances in a very cool place so as to render them hard and easily pulverable. Where this work has to be done on a large scale it is advisable to carry on the operation in the winter time.

Transition Stages of Resinous Bodies and their Nomenclature.—A few words as to the nomenclature of the resins, the transition of one form of resin into another, and their mutual relation. Since we use names—such as dammar, copal, elemi, kino, etc.—which do not specially indicate any special resin, it follows, as a matter of course, that confusion is liable to occur. Special mention will be made in Part II. of this indefinite nomenclature, with particular reference to the transition stages between kino and dragon's-blood, bdellium and myrrh, turpentine resins and dammar or copal; the, to some extent, nearly allied names, such as: *resina caranna*, gomart gum, *resina kikekunemalo*, anime, *tacamahac*, elemi, etc. The variations in the names of commercial grades also frequently lead to much confusion.

PART II.

INTRODUCTION.

BEFORE proceeding to specially consider the various resinous substances separately, a few general remarks are necessary.

In dealing with the estimation of the acid, ester, and saponification values, the expression "usual method" implies the method performed in the same manner as in the case of fats—*i. e.* the Hübl method—without any special modification. Thus the acid-value determination consists of: solution in alcohol, and direct titration with $\frac{n}{2}$ alkali and phenolphthalein; the saponification-value method is: boiling for half an hour under a reflux condenser, and titrating back after cooling, the reagents used being alcoholic $\frac{n}{2}$ alkali, and aqueous $\frac{n}{2}$ sulphuric acid. The ester value is found by calculation, as already described in Part I.

The estimation of "matters soluble in petroleum ether" by the Hirschsohn method, so frequently referred to, is effected by extracting the substance with petroleum spirit, of boiling-point 40° , 60° , or 80° C., and drying the extract at 120° C. until of constant weight. In other cases the solution is evaporated at 17° C., and the residue weighed till constant. Where the above temperatures are referred to in this connection, they must be taken to express the same meanings as here involved; and all specific gravities refer to 15° C., unless any other temperature is specially mentioned.

The following practical hint may be given in connection with the analysis of resins and the necessary weighings

herein :—In the case of such resins as soft elemi, storax, etc., which are of a greasy or balsamic character, weighing out into narrow-necked litre flasks (for cold and fractional saponification) is inconvenient by reason of the resin adhering to the rim and taking a long time to run down. It is then better to place a small quantity of the resin on a tared watch glass, and weigh the whole, take up about 1 grm. by means of a small glass rod, and insert rod and all into the flask; the loss in weight of the watch glass and contents then gives the quantity of resin taken for analysis. Thus the above-named inconvenience is avoided. The preparation of average samples has already been discussed under axiom XXIII. (Part I.).

Definitions.

1. The *acid value* (direct and indirect) = the number of mgrms. KHO combined by the free acid in 1 grm. of resin during direct or back titration.

2. The *acid value of the volatile portion* = the number of mgrms. KHO combined by 500 grms. of distillate obtained from 0.5 grm. of gum resin (ammoniacum, galbanum) by distillation with steam.

3. The *saponification value* (hot and cold) = the number of mgrms. KHO combined by 1 grm. of resin in hot or cold saponification.

4. The *resin value* = the number of mgrms. KHO combined by 1 grm. of certain resins and gum resins on cold fractional saponification with alcoholic alkali by itself.

5. The *total saponification value* (fractional saponification) = the total number of mgrms. KHO combined by 1 grm. of certain resins and gum resins on cold fractional saponification with alcoholic and aqueous alkali in succession.

6. The *gum value* = the difference between the total saponification value and the resin value.

7. The *ester value* = the difference between the saponification value and the acid value.

8. The *acetyl value* = the difference between the acetyl saponification value and the acetyl acid value.

9. The *carbonyl value* = the percentage of carbonyl oxygen in the substance taken.

10. The *methoxyl value* = the amount of methoxyl furnished by 1 grm. of resin.

The following abbreviations (which denote the methods used) have been employed through this second part of the present work, with a view of securing their general adoption :—

Thus—

S.-Z. d.	= Acid value (Säurezahl), direct.
S.-Z. ind.	= Acid value, indirect (by back titration).
S.-Z. f.	= Acid value of volatile (flüchtige) constituents.
E.-Z.	= Ester value (Esterzahl).
V.-Z. h	= Saponification value, hot (Verseifungszahl heiss).
V.-Z. k	= Saponification value, cold (kalt).
H.-Z.	= Resin value (Harzzahl).
G.-V.-Z.	= Total saponification value (Gesamt-Verseifungszahl).
G.-Z.	= Gum value (Gummizahl).
C.-Z.	= Carbonyl value (Zahl).
M.-Z.	= Methoxyl value (Zahl).
A.-Z.	= Acetyl value (Zahl).
A.-S.-Z.	= Acetyl acid value.
A.-V.-Z.	= Acetyl saponification value.
A.-E.-Z.	= Acetyl ester value.

The calculations are based on the new table of atomic weights drawn up by Landolt, Ostwald, and Seubert, and adopted by the German Chemical Society.

A. BALSAMS

1. Canada Balsam.

Balsamum Canadense.

Origin and Habitat.—*Abies balsamea*, DC. (Coniferæ). North America.

Chemical Constituents.—Levo-rotatory ethereal oil, 18·6 per cent.; resin soluble in alcohol, 46 per cent.; resin sparingly soluble in alcohol, 33·4 per cent.; caoutchouc, 4 per cent.; bitter principles, extractives, traces of acetic acid, 4 per cent. (Bonastre).

General Properties and Commercial Varieties.—Canada balsam is perfectly clear, pale yellow (almost greenish) in colour, and slightly fluorescent. The odour is agreeably aromatic, the flavour bitter, and it yields a bitter principle when treated with hot water. The balsam is only partially soluble in absolute alcohol. (See also under Turpentine, Tereb. argentoratensis, Strassburg T.)

Adulterants.—Colophony, Venice turpentine.

Analysis.—In general the available analytical data are meagre. Hirschsohn found that Canada balsam is soluble in petroleum ether, except for a small residue, but that the subsequent addition of more solvent produced turbidity.

A. Kremel found—

$$\begin{array}{l} \text{Acid value, direct (S.-Z. d.)} = 83\cdot0 \\ 81\cdot3 \end{array}$$

by dissolving about 1 grm. in strong alcohol and titrating direct with alcoholic $\frac{n}{2}$ potash. The ester value and saponification value were not examined.

F. Dietze found—

	I.	II.	III.
Acid value, d. (S.-Z. d.) . . .	84.89	85.93	84.40
Ester value (E.-Z.)	4.54	9.83	9.00
Saponification value, hot (V.-Z. h.)	89.43	95.76	93.40

the acid value being determined by the method practised by Kremel, and the saponification value by the "usual method" (see Introduction to Part II.).

E. Dieterich found—

S.-Z. d. = 84.0–86.8 (Kremel method).

Solubility in—

Chloroform	} complete.
Acetic ether	
Benzol	
Ether	} almost to quite complete.
Oil of turpentine	
90 per cent. alcohol, up to 90.90–93.58 per cent.	
Petroleum ether, 83.46–92.73 per cent.	

The iodine values obtained by E. Dieterich are omitted here, as is the case with all iodine values relating to resinous products, such values being unreliable, as already stated in Part I.

The methoxyl value was found = 0 by Gregor and Bamberger.

(For the detection of colophony in resins and balsams by the Storch-Morawski method, see under Colophony.)

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Copaiba Balsam.

Balsamum Copaivæ (D. A. III.).

Origin.—Various *Copaifera*, such as *Copaifera officinalis* and *guianensis*, etc.; Cæsalpinaceæ.

Habitat.—South America, East Indies, Africa.

Chemical Constituents.—Ethereal oil, 40–60 per cent.; resin, 60–40 per cent.

The ethereal oil corresponds to the formula $C_5H_8 = C_{15}H_{24}$ (Berthelot), or $C_{20}H_{32}$ for Para balsam (Engländer.) The resin is soluble in alcohol, benzol, and amyl alcohol, and chiefly consists of amorphous acids—copaibic acid ($C_{20}H_{30}O_2$), however, being crystalline (Schweitzer); Para balsam contains oxycopaibic acid, $C_{20}H_{28}O_3$ (Fehling); Maracaibo balsam contains metacopaibic acid, $C_{22}H_{34}O_4$ (Strauss); and bitter principles have been detected in all the varieties of this balsam.

General Properties and Commercial Varieties.—Of the two principal classes of copaiba balsam, the thick and the thin, Maracaibo (Venezuela) balsam may be taken as representing the former type, and Para (Maranhão) balsam the more fluid class, the other kinds being mostly intermediate. The majority, like Gurjun balsam, exhibit strong green fluorescence. The chief commercial varieties are Maracaibo and Para. Latterly Maturin balsam has been recommended as a substitute for the thick officinal Maracaibo balsam, as was formerly the case with Angostura and Carthagena balsams. All the varieties have a very strong and aromatic odour, and a bitter, irritant taste. Bahia, Carthagena, Surinam, Angostura, and “West African” (Illurin, Antilles) balsams are now seldom found in commerce. According to Hartwich, a balsam (“baume à cochon”) similar in action to copaiba is obtained from *Hedwigia balsamifera* (Burseraceæ family), and *Humiria*

floribunda yields a balsam which smells like benzoin and is used as a remedy for gonorrhœa (Hartwich).

Adulterants, etc.—The officinal balsams are adulterated with Gurjun balsam, fatty oils (ricinus oil, olive oil), storax, colophony, turpentine, sassafras oil,¹ oil of turpentine, paraffin oil, etc., whilst the other balsams are frequently mistaken for, or adulterated by, one another. Maracaibo balsam is mostly falsified with thin Para balsam.

Analysis.—With the exception of Peruvian balsam there is probably no balsam that has been so widely examined as copaiba, nearly all the known varieties, such as Angostura, Bahia, Carthagena, Maracaibo, Maturin, Gurjun, Para, Surinam, and West African balsams, having been tested. That Maracaibo balsam, being the officinal medicament (D. A. III.), has been examined with particular frequency, goes almost without saying. The main reason for the great variations in the results obtained by different workers is the almost entire absence of a really pure balsam among the commercial grades, adulteration being both frequent and varied. Mention of this circumstance has been made by Gehe & Co., *The Oil Paint and Drug Reporter*, and (more recently) by K. Dieterich. An innumerable array of qualitative reactions and modifications of same has been recorded by Ulex, Wagner, Maisch, Procter, Guibourt, Dierbach, Raleigh, Chrestien, König, Lowe, Gerber, Rose, Thorn, Gutnik, Vigne, Vallet, Redwood, Hager, Wimmel, Gehe & Co., Enell, Muter, Hirschsohn, Maupy, and others. The first large and comprehensive work on the various copaiba balsams was published by E. Praël, who also determined the content of resins and ethereal oils; and subsequently, quantitative methods for determining the acid, ester, and saponification

¹ This oil is, however, dearer than copaiba balsam, and is therefore unlikely to figure in practice as an adulterant of the latter.

values, and the sp. gr., were introduced by A. Kremel. The utility of these values is the subject of much difference of opinion, for whereas Beckurts and Brüche declare in favour of the iodine value, others—Wimmel, Gehe & Co., and more recently, K. Dieterich—think little of this test. Nearly all authors, however, are unanimous in recommending the quantitative determination of the acid, ester, and saponification values, and the fixing of a standard of specific gravity; but so long as pure and uniform products are unobtainable in commerce no reliance can be placed on the Hager optical rotation method (Maracaibo balsam dextro-, nearly all commercial balsams levo-rotatory); the acid test as given in the German Pharmacopœia (D. A. III.), or by Enell; the ammonia test of Gehe & Co., Wimmel, and Bosetti; or the Grote agitation test. The only possible way of valuing the balsams is by making quantitative determinations of the above-named constants, and by fixing limits of fluctuation within which variation is permissible to the various balsams. This plan has been latterly recommended by Caesar & Loretz, and by Gehe & Co., as a progressive step, though, of course, as pointed out by Thoms, methods so imperfect as those given in the German Pharmacopœia are inapplicable. With regard to fixing a margin of permissive variation, this will have to be postponed, Gehe & Co. having found that some adulterated balsams give values within the limits set up by K. Dieterich for the pure products; and it will not be until we can obtain samples of undeniable purity that reliable limits can be laid down for copaiba balsams. On the other hand, the author differs from Gehe & Co., in that he attributes a merely subordinate importance to the qualitative tests with ammonia and colophony (Bosetti's method). Owing to the variable proportion of ethereal oil and copaiba resin, the method prescribed for determining these constituents by the British

Pharmacopœia has as little to recommend it as the iodine value test. However, it seems advisable to determine in the various separate balsams the percentage of matters extractable by various solvents, as was formerly done with nearly all known resins by E. Dieterich, in continuance of the values obtained by Hirschsohn, von Schmidt and Erban, Muter, Präel, and others. The qualitative reactions and iodine values have been omitted from the present work, for reasons already stated. The Mauch method for observing the colour reactions furnished by the ethereal oil extracted by chloral hydrate is perhaps an improvement, so far as the accuracy of the colour reactions themselves; although these, like others of the same class, are always more or less unreliable. Nevertheless, the value of his method in showing that ethereal oils can be easily isolated by chloral hydrate should not be under-estimated.

Gregor and Bamberger's methoxyl values cannot be quoted, the authors having omitted to state which balsams were examined.

2. Angostura Copaiba Balsam.

The information available about this balsam is rather scanty.

Präel found—Sp. gr. 0·980–1·009; resin, 59·90 per cent.; ethereal oil (sp. gr. 0·906), 40·10 per cent.

Beckurts and Brüche found—

Acid value, d. (S.-Z. d.)	. . .	99·6
Ester value (E.-Z.)	. . .	<i>nil</i>
Saponification value, hot (V.-Z. h.)	99·6	
Sp. gr.	1·022

The value S.-Z. d. was determined by titrating the solution of 1 grm. balsam in 95 per cent. alcohol, with alcoholic $\frac{n}{2}$

potash and phenolphthalein; the value V.-Z. h. by boiling 1 grm. for fifteen minutes with 25 c.c. alcoholic $\frac{n}{2}$ potash under a reflux condenser, and titrating back with $\frac{n}{2}$ sulphuric acid.

Gehe & Co. seek to have the Angostura balsam included with Maracaibo balsam in the German Pharmacopœia (D. A. III.). They are equivalent, but the first-named gives a red coloration in the D. A. III. acid test. According to Beckurts and Brüche no such coloration occurs, the balsam behaving in a normal manner.

The opinion of the last-named workers was that the qualitative and quantitative tests indicated an adulterated sample of Angostura balsam.

It is evident from the different results obtained by Beckurts and Brüche, and by Gehe & Co., that variations exist in these products. The results must therefore be accepted *cum grano salis*, and are of the less importance in that this balsam is now no longer met with in commerce.

The author has examined several Angostura balsams by the methods proposed by himself for Maracaibo balsam, and obtained the following values:—

	I.	II.	III.
Acid value, d. (S.-Z. d.)	$\begin{cases} 79\cdot52 \\ 80\cdot70 \end{cases}$	$\begin{cases} 83\cdot00 \\ 83\cdot50 \end{cases}$	$\begin{cases} 75\cdot87 \\ 76\cdot32 \end{cases}$
Ester value (E.-Z.)	$\begin{cases} 16\cdot24 \\ 17\cdot38 \end{cases}$	$\begin{cases} 8\cdot36 \\ 7\cdot94 \end{cases}$	$\begin{cases} 16\cdot07 \\ 16\cdot19 \end{cases}$
Saponification value, cold (V.-Z. k.)	$\begin{cases} 95\cdot76 \\ 98\cdot08 \end{cases}$	$\begin{cases} 96\cdot36 \\ 91\cdot44 \end{cases}$	$\begin{cases} 91\cdot54 \\ 92\cdot51 \end{cases}$

The acid test of the Pharmacopœia was not tried. That the above values differ from these obtained by Beckurts and Brüche confirms the latter's view that they were working with an adulterated sample.

(N.B.—The bibliographical references relating to all the various copaiba balsams will be found on p. 83.)

3. Bahia Copaiba Balsam.

Very few analytical data are available on the subject of this variety.

Praël found—Sp. gr. 0·980; resin content, 59·80 per cent.; ethereal oil (sp. gr. 0·988), 40·20 per cent.

Beckurts and Brüche found—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	73·0	97·5
Ester value (E.-Z.) . . .	<i>nil</i>	15·2
Saponification value, hot (V.-Z. h.)	73·0	112·7
Sp. gr.	0·962	1·031 (!)

by the usual method. On the basis of further tests of a qualitative nature, the authors believed both samples to be of questionable purity. As Bahia balsam is now rarely met with in commerce, the above fluctuating values are merely cited without, in the meantime, being credited with any practical importance.

K. Dieterich has also examined Bahia balsam by the same methods as he applied to Maracaibo balsam, and obtained the following results:—

I. Balsam of undoubted purity, from the author's own collection—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	81·09	81·27
Ester value (E.-Z.) . . .	5·08	6·08
Saponification value, cold (V.-Z. k.)	86·17	87·32

II. An undoubtedly adulterated sample from Hamburg—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	64·19	64·25
Ester value (E.-Z.) . . .	1·76	2·60
Saponification value, cold (V.-Z. k.)	65·95	66·85

Balsam No. I. was entirely soluble in alcohol, except for a slight turbidity, whilst the No. II. sample was thinner, and only partly soluble, to a turbid solution, in alcohol, numerous

large flakes being left behind. The former was undoubtedly pure, but the latter just as certainly adulterated (probably with vaseline oil).

4. Carthagena Copaiba Balsam.

For this balsam, Praël found—Sp. gr. 0·958; resin content, 46·20 per cent.; ethereal oil (sp. gr. 0·904), 53·80 per cent.

Kebler found—Oil (b.p. 250°–265° C.), 53 per cent.

Beckurts and Brüche found—

Acid value, d. (S.-Z. d.)	88·9
Ester value (E.-Z.)	<i>nil</i>
Saponification value, hot (V.-Z. h.)	88·9
Sp. gr.	0·988

the S.-Z. and V.-Z. values by the method used on Angostura balsam, *i.e.* the usual method.

Gehe & Co. recommend this balsam also as a substitute for Maracaibo balsam, from which, like Angostura balsam, it differs (according to their report) by the positive result (red coloration) given in the D. A. III. acid test.

The author has examined several samples of Carthagena balsam by his own method (see Maracaibo balsam), and obtained the following values:—

	I.	II.	III.
Acid value, d. (S.-Z. d.)	{ 49·00	62·30	87·75
	{ 49·40	62·76	88·23
Ester value (E.-Z.)	{ 56·20	41·15	4·55
	{ 87·17	40·90	4·67
Sapon. value, cold (V.-Z. k.)	{ 105·20	103·45	92·30
	{ 106·57	103·57	92·90

The sample No. III. agrees well with the figures of Beckurts and Brüche, but Nos. I. and II. seem doubtful products.

5. Maracaibo Copaiba Balsam.

This, now officinal, thick balsam has frequently been examined quantitatively.

Praël found—Sp. gr. 0·983–0·995; resin, 54·80–61·43 per cent.; ethereal oil (sp. gr. 0·897–0·905), 38·57–45·20 per cent.

A. Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	73·0–75·0	76·0

by direct titration with alcoholic $\frac{n}{2}$ potash. The ester and saponification values were not determined.

Beckurts and Brüche found—

	I.	II.	III.
Acid value, d. (S.-Z. d.)	98·0	79·3	95·8
Ester value (E.-Z.)	<i>nil</i>	19·7	5·4
Sapon. value, h. (V.-Z. h.)	98·0	99·0	100·8
Sp. gr.	0·995	0·973	0·991

by the usual methods.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	76·52–94·90
Ester value (E.-Z.)	0·47–8·75
Sapon. value, h. (V.-Z. h.)	80·27–100·80

Solubility in—

Ether	}	complete.
Chloroform		
Petroleum ether		
Oil of turpentine		
Carbon di-sulphide	}	almost complete.
Alcohol (90 per cent.)		
Acetic ether		

The usual methods were employed for determining the constants, except that in the saponification test the liquid was concentrated to expel the alcohol, and was then titrated after re-dilution.

L. Maupy proposed to detect ricinus (castor) oil in copaiba balsam by a test based on the fact that when ricinus oil is subjected to dry distillation in presence of caustic potash or soda, the products include sebacic acid and capryl alcohol. The sebacic acid is isolated by decomposing the resulting soap with mineral acids, and is readily soluble in hot water. In testing for ricinus oil, 10 grms. of the suspected copaiba are heated with 10 grms. of dry caustic soda, the ethereal oil being driven off in the form of white vapours. When ricinus oil is present, a decided odour of capryl alcohol is noticeable. The residue, which, in the meantime, will have separated into an upper wax-like mass and an inferior, liquid stratum, is then stirred with a glass rod, left to cool, treated with 50 grms. of water, heated up, and passed through a wet filter. The sebacic acid separates out from the filtrate, and can be converted into its white lead salt by treating the slightly acid solution in boiling water with lead acetate.

Recently the author has worked out a method for investigating the copaiba balsams, and drawn up a scheme showing the influence exerted by various adulterants on the results.

With normal Maracaibo balsam the following values were obtained —

Sp. gr. 0.980-0.990
Acid value, d. (S.-Z. d.) 75.0-85.0
Ester value (E.-Z.) 3.0- 6.0
Saponification value, cold (V.-Z. k) . .	. 80.0-90.0

The K. Dieterich method for determining these values is carried out as follows:—

(a) *Acid value, direct.*—One grm. of balsam is dissolved in 200 c.c. of 96 per cent. alcohol, and titrated with alcoholic $\frac{n}{2}$ potash in presence of phenolphthalein until a red coloration

is obtained. The volume of alkali consumed, multiplied by 28·08, gives the acid value.

(b) *Saponification value, cold.*—One grm. of balsam is placed in a stoppered 1 litre flask and suffused with 20 c.c. of $\frac{n}{2}$ alcoholic potash and 50 c.c. of benzine (sp. gr. 0·700). After leaving the closed flask for twenty-four hours at room temperature, the contents are diluted with strong alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The saponification value is obtained by multiplying the volume (c.c.) of combined KHO by 28·08.

(c) The *ester value* is found by calculation.

The author has examined a number of old and adulterated balsams by this method, and has collected the results into the subjoined table :—

Copaiba Balsam.	Sp.gr. at 15° C.	Acid Value (S -Z. d.).	Saponification Value (V.-Z. k.).	Ester Value (E.-Z.).
Maracaibo D. A. III. (the balsam used in the following adulterations)	0·985	77·31— 78·12	80·32— 83·41	3·01— 5·29
Maracaibo D. A. III. (3 years old (from the author's collection)	1·001	93·88— 94·33	97·56—101·35	3·68— 7·02
D.A.III. +10% Gurjun balsam	0·987	70·20— 71·13	76·35— 78·64	6·15— 7·51
„ +20% „ „	0·985	62·68— 63·90	71·56— 71·83	7·93— 8·88
„ +30% „ „	0·983	55·92— 56·14	75·09— 82·03	19·13—25·89
„ +10% Ordy. olive oil	0·982	71·87— 72·11	112·48—113·55	40·61—41·44
„ +20% „ „	0·974	63·39— 64·66	104·74—104·87	40·21—41·35
„ +30% „ „	0·967	58·46— 58·56	122·86—124·80	64·40—66·24
„ +10% Ricinus (castor) oil	0·986	68·43— 69·89	93·79— 97·96	25·36—28·07
„ +20% „ „	0·983	63·14— 63·32	102·94—105·46	39·80—42·14
„ +30% „ „	0·980	56·80— 58·19	114·15—115·95	57·35—57·76
„ +10% Sassafras oil	0·994	69·98— 70·75	75·14— 75·44	4·69— 5·16
„ +20% „ „	1·001	61·96— 64·13	68·40— 68·56	4·43— 6·44
„ +30% „ „	1·010	55·73— 57·00	59·30— 62·14	3·57— 5·14

Copaiba Balsam.	Sp gr. at 15° C.	Acid Value (S.-Z. d.).	Saponification Value (V.-Z. k.).	Ester Value (E.-Z.).
D.A.III. + 10% Oil of turpentine	0.986	69.43— 70.69	79.74— 86.64	10.31— 15.95
“ + 20% „ „	0.981	63.56— 63.98	76.97— 75.75	12.19— 12.99
“ + 30% „ „	0.972	56.58— 57.29	70.00— 70.77	13.42— 13.48
“ + 10% Venice turpen- tine	0.992	81.14— 82.74	85.70— 90.58	4.56— 7.84
“ + 20% „ „	0.996	85.44— 85.76	89.76— 90.59	4.32— 4.83
“ + 30% „ „	0.999	88.36— 89.07	95.06— 97.80	6.70— 8.73
“ + 10% Colophony	0.995	85.03— 85.40	95.13— 102.34	10.10— 16.94
“ + 20% „ „	1.003	95.91— 97.47	102.65— 103.03	5.56— 6.74
“ + 30% „ „	1.018	105.70— 106.25	110.49— 111.17	4.79— 4.92
“ + 10% Liquid paraffin	0.975	68.90— 69.41	75.98— 77.09	7.08— 7.68
“ + 20% „ „	0.963	61.41— 62.41	70.67— 72.38	9.26— 10.17
“ + 30% „ „	0.951	54.55— 56.11	78.09— 79.04	22.93— 23.54

Consequently the added adulterants modify the constants of normal Maracaibo balsam in the following manner:—

1. Gurjun balsam increases sp. gr., lowers acid value, and raises saponification and ester values.

2. Olive oil reduces sp. gr. and acid value, but considerably increases the ester and saponification values.

3. Sassafras oil heightens sp. gr., lowers acid and saponification values, leaving ester value almost unchanged.

4. Oil of turpentine reduces sp. gr., acid value, and saponification value, but considerably increases ester value.

5. Venice turpentine increases sp. gr., acid value, and saponification value, leaving ester value almost unchanged.

6. Colophony greatly increases sp. gr. and acid value. No definite conclusions deducible from ester and saponification values.

7. Liquid paraffin reduces sp. gr. and acid value, increases ester value, but leaves saponification value about normal.

8. Ricinus (castor) oil reduces sp. gr. and acid value, con-

siderably increasing ester and saponification values, like olive oil (No. 2).

9. Resinified old balsam. The acid and saponification values and sp. gr. are greatly increased, analogous to the influence of colophony (No. 6).

Thus, when abnormalities are detected in Maracaibo balsam, an approximate conclusion can be drawn from the above method as to whether the sample is old, resinified, or adulterated, taking the following indications as a guide:—

The Maracaibo balsam exhibits in comparison with the normal—	Thus foreshadowing the presence of—
I. Unduly high sp. gr. Do. low acid value. Do. high ester value. Do. do. saponification value.	} Gurjun balsam.
II. Unduly high sp. gr. Do. acid value. Do. saponification value.	
III. Unduly low sp. gr. Do. do. acid value. Do. high ester value. Do. do. saponification value.	} Olive oil or ricinus oil.
IV. Unduly low sp. gr. Do. do. acid value. Do. do. saponification value. Do. high ester value.	
V. Unduly high sp. gr. Do. acid value.	} Colophony.
VI. Unduly low sp. gr. Do. do. acid value. Do. high ester value.	
VII. Unduly high sp. gr. Do. low acid value. Do. do. saponification value.	} Sassafras oil.
VIII. Unduly high sp. gr. Do. acid value. Do. saponification value.	

The value affording the least guidance is the sp. gr., and for this reason it is highly desirable to fix a relatively small margin of deviation for the sp. gr. of officinal Maracaibo balsam. The author has proposed 0.980–0.990. The values (*e.g.* acid value) obtained by Kremel, E. Dieterich, Beckurts and Brüche can only in part be compared with those of K. Dieterich owing to the difference in the methods employed. Of course the foregoing scheme of adulterations cannot serve as a guide unless the author's methods of determination be used. The existing method of testing Maracaibo in the German Pharmacopœia, though quantitative, is inaccurate and unsuitable.

As already stated, Gehe & Co. consider the limits of permissive deviation laid down by the author too wide, or as not always permitting the detection of adulterations, they having found that mixtures of Maracaibo and Para balsam with colophony furnish values within the said limits. Gehe & Co. believe—in opposition to the author—that particular value attaches to the Bosetti test, namely, melting the balsam with 30 per cent. of colophony, adding 10 per cent. ammonia, and observing the result as regards gelatinisation, the absence of which phenomenon is considered to indicate purity. The author believes that, as with Peruvian balsam, the accuracy of this assumption cannot be proved until the test has been made with samples of known purity taken direct from the parent tree. At present none of the existing values have been obtained from balsams of unimpeachable purity, so that even the limits given by the author (see also Para balsam), being derived from relatively impure commercial specimens, can only be *à priori* regarded as of relative accuracy. Gehe & Co. state—which is particularly important—that Gurjun balsam is less largely used than thin Para balsam for adulterating Maracaibo balsam.

6. Maturin Copaiba Balsam.

Praël found—sp. gr. 0·983 ; resin, 55 per cent. ; ethereal oil (sp. gr. 0·898), 45 per cent.

A. Kremel found—acid value, d. (S.-Z. d.), 77·1, but did not determine the ester and saponification values.

F. Dietze found, by the usual methods—

Acid value, d. (S.-Z. d.)	78·17
Ester value (E.-Z.)	4·26
Saponification value, h. (V.-Z. h.)	82·43

He recommended this balsam as a substitute for the officinal variety (Maracaibo), a proposal which seems all the more justifiable in that the characteristic values of the two agree very well, thus differing from the other varieties of copaiba.

The author treated Maturin balsam by his aforesaid method, and obtained the following results :—

	I.	II.
Acid value, d. (S.-Z. d.)	78·52	82·73
Ester value (E.-V.)	12·86	9·29
Saponification value, cold (V.-Z. k.)	91·38	92·02

figures which agree well with those of other workers.

7. Gurjun (East Indian) Copaiba Balsam.

This balsam, which is used to adulterate Maracaibo balsam, has been examined by several authors.

A. Kremel found—

	I.	II.	III.	IV.
Acid value, d. (S.-Z. d.)	20·0	19·3	14·2	5·8

by the usual method.

Kebler found—sp. gr., at 15° C., 0·9796 ; ethereal oil (b.p. 254–263° C.), 54 per cent.

Beckurts and Brüche found—

Acid value, d. (S.-Z. d.)	8·7
Ester value (E.-Z.)	<i>nil</i>
Saponification value, h. (V.-Z. h.)	8·7
Sp. gr.	0·955

E. Dieterich found—

Acid value, d. (S.-Z. d.)	6·5 – 7·4
Ester value (E.-Z.)	10·30–11·20
Saponification value, h. (V.-Z. h.)	16·80–18·60

Solubility in—

Alcohol (90 per cent.)	} complete.
Chloroform	
Acetic ether	
Benzol	
Oil of turpentine	} incomplete.
Ether	
Petroleum ether	
Carbon di-sulphide	

the usual methods being employed, subject to the same authority's modification, already cited under Maracaibo balsam. More recently the present author has applied his own method to Gurjun balsam, as well as the other varieties of copaiba, and found—

Sp. gr.	0·955–0·965
Acid value, d. (S.-Z. d.)	5·0–10·0
Ester value (E.-Z.)	1·0–10·0
Saponification value, cold (V.-Z. k.)	10·0–20·0

the following values being obtained on a later occasion :—

	I.	II.
Acid value, d. (S.-Z. d.)	{ 10·80	10·64
	{ 10·98	10·77
Ester value (E.-Z.)	{ 14·00	14·83
	{ 15·37	15·00
Saponification value, cold (V.-Z. k.)	{ 24·80	25·47
	{ 26·35	25·77

These figures agree with those of Beckurts and Brüche and E. Dieterich, but not with the high acid values found in some cases by Kremel.

Gregor and Bamberger found the methoxyl value = 0.

8. Para Copaiba Balsam.

Praël found—sp. gr. 0·916–0·989 ; resin, 23·87–59·53 per cent.; ethereal oil (sp. gr. 0·98·8–0·902), 40·47–76·13 per cent.

A Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	29·6 (!)	78·2

by the usual method, but did not test the ester and saponification values. The low acid value of No. 1 Kremel himself considered questionable.

Beckurts and Brüche found—

	I.	II.
Acid value, d. (S.-Z. d.)	87·0	38·1 (!)
Ester value (E.-Z.)	0·0	2·9 (!)
Saponification value, hot (V.-Z. h.)	87·0	41·0 (!)
Sp. gr.	0·984	0·949

all by the usual method. The values marked (!) were regarded by the authors themselves as incorrect, and probably attributable to adulterations in the sample.

Kebler found—sp. gr. 0·9254 ; oil (b.p. 258–270° C.), 90 per cent.

E. Dieterich found, by the method adopted for Maracaibo balsam—

Acid value, d. (S.-Z. d.)	29·40–65·80
Ester value (E.-Z.)	1·90
Saponification value, hot (V.-Z. h.)	31·30–67·70

Solubility in—

Ether	}	complete.
Chloroform		
Benzol		
Oil of turpentine		
Alcohol (90 per cent.)	}	almost complete.
Acetic ether		
Petroleum ether		
Carbon di-sulphide		

K. Dieterich found—

Sp. gr.	0.95– 0.97
Acid value, d. (S.-Z. d.)	40.0 –60.0
Ester value (E.-Z.)	2.0 – 8.0
Saponification value, cold (V.-Z. k.).	30.0 –60.0

and subsequently—

	I.	II.
Acid value, d. (S.-Z. d.).	{ 49.47	61.62
	{ 49.92	61.86
Ester value (E.-Z.)	{ 15.15	9.06
	{ 18.06	8.89
Saponification value, cold (V.-Z. k.)	{ 64.62	70.68
	{ 67.98	70.75

Apart from the somewhat higher ester value, these figures correspond with the others given above.

These last-named values were obtained by the author's own method, already described. He proposed to constitute the first set a standard for good Para balsam, but, according to Gehe & Co., this is inadmissible.

The author has, in this case also, examined the influence exerted by adulteration on the normal values—

Copaiba Balsam.	Sp. gr.	Acid Value, d. (S.-Z. d.).	Sapon. Value, cold (V.-Z. k.).	Ester Value (E.-Z.).
Para + 10% Gurjun balsam	0.971	41.59—43.27	62.54— 70.13	20.95—26.86
„ + 20% „ „	0.974	38.13—38.97	73.33— 74.93	35.20—35.96
„ + 30% „ „	0.974	34.25—34.30	71.85— 71.94	37.60—37.64
„ + 10% Olive oil (ordy.)	0.971	41.36—46.02	86.26— 89.85	43.83—44.90
„ + 20% „ „	0.964	37.40—38.22	90.89— 97.85	53.49—59.63
„ + 30% „ „	0.955	35.44—37.05	102.40—103.26	66.21—66.96
„ + 10% Ricinus (castor) oil	0.972	40.83—41.34	93.45— 94.54	52.62—53.20
„ + 20% „ „	0.970	37.55—38.07	89.28— 92.33	51.73—54.26
„ + 30% „ „	0.966	38.89—38.97	97.01— 97.95	58.12—58.98
„ + 10% Sassafras oil	0.985	45.45—45.98	53.67— 54.44	8.22— 8.46
„ + 20% „ „	0.985	43.84—44.90	47.31— 47.98	3.08— 3.47
„ + 30% „ „	0.995	39.83—40.29	44.81— 46.65	4.98— 6.36
„ + 10% Oil of turpentine	0.973	42.44—42.97	70.26— 75.04	27.82—32.07
„ + 20% „ „	0.969	41.18—41.33	59.01— 59.04	17.71—17.83
„ + 30% „ „	0.960	39.76—40.12	51.10— 52.45	11.34—12.33
„ + 10% Venice turpentine	0.980	53.69—54.14	70.99— 71.17	17.03—17.30
„ + 20% „ „	0.982	62.82—63.18	72.17— 75.96	9.35—12.78
„ + 30% „ „	0.986	68.99—69.02	81.81— 82.99	12.82—13.97
„ + 10% Colophony	0.982	57.92—60.16	68.92— 70.98	10.82—11.00
„ + 20% „ „	0.991	75.56—75.72	89.80— 91.21	14.24—15.49
„ + 30% „ „	1.000	90.33—91.67	93.13— 94.12	2.45— 2.80
„ + 10% Liquid paraffin	0.962	39.95—41.68	66.83— 68.49	26.81—26.88
„ + 20% „ „	0.951	33.86—34.09	55.35— 57.66	21.49—23.57
„ + 30% „ „	0.935	30.79—31.11	51.89— 53.46	21.10—22.35

The effects of adulterants on normal Para balsam may be stated as follows:—

1. Gurjun balsam increases the sp. gr., reduces the acid value, and considerably heightens the saponification and ester values.

2. Olive oil, ricinus oil, and other fatty oils lower the sp. gr. and acid value, but considerably increase the saponification and ester values.

3. Sassafras oil heightens the sp. gr., but depresses the acid and saponification values.

4. Oil of turpentine lowers the sp. gr. and acid value, but largely increases the ester value.

5. Venice turpentine raises the sp. gr. and the acid, ester, and saponification values.

6. Colophony raises the sp. gr., acid value, and saponification value.

7. Liquid paraffin reduces the sp. gr., greatly lowers the acid value, and considerably increases the saponification value.

In the case of abnormal values furnished by Para balsam, the author's method affords a means of forming a relatively accurate opinion as to whether the sample is old, resinified, adulterated, or altered in some other way. The following indications will serve as a guide :—

When Para balsam exhibits the following abnormalities :—	The presence of the subjoined bodies may be presumed—
I. Unduly high sp. gr. Do. low acid value. Do. high saponification value (cold). Very high ester value.	} Gurjun balsam.
II. Unduly low sp. gr. Do. acid value. Very high ester value. Do. saponification value.	} Olive oil, ricinus oil, and fatty oils generally.
III. Unduly high sp. gr. Do. low acid value. Do. do. saponification value.	} Sassafras oil.
IV. Unduly low sp. gr. Do. acid value. Very high ester value.	} Oil of turpentine.
V. Unduly high sp. gr. Do. acid value. Do. ester value. Do. saponification value.	} Venice turpentine.

VI. Unduly high sp. gr.	}	Colophony.
Do. acid value.		
Do. saponification value.		
VII. Unduly low sp. gr.	}	Liquid paraffin.
Very low acid value.		
Do. high ester value.		

With regard to sp. gr., the remarks already passed on Maracaibo balsam also apply here.

9. Surinam Copaiba Balsam.

Origin.—*Copaifera guianensis* and other *Copaiferae*.

Habitat.—Surinam.

Chemical Constituents.—Copaibic acid, ethereal oil, 78 per cent. (Pool).

General Properties and Commercial Varieties.—The balsam is a clear, pale yellow, non-opalescent liquid, resembling olive oil, and miscible in all proportions with ether, chloroform, petroleum ether, and carbon di-sulphide. In Surinam the balsam is known as “hoopal” or “hooper” oil, on account of the wood being used for hooping sugar casks. This balsam is seldom met with in commerce.

Adulterants.—Other balsams.

Analysis.—Pool investigated this balsam, with the following results:—

The sp. gr. is 0.942, and the balsam is miscible with petroleum ether, chloroform, ether, and carbon di-sulphide in all proportions. Mixed in equal proportion with alcohol it turns turbid, but dissolves when the alcohol is increased four or five fold. The (hot) saponification value is 34. One and a half grm. of balsam combines with 94 mgrms. of iodine. The balsam contains 78 per cent. of a colourless ethereal oil of sp. gr. 0.94 and b.p. 250°–260° C. The residual resin left after distilling off this oil was extracted with dilute

alcohol, the evaporated extract leaving crystals of copaibic acid of m.p. 130°C . It differs from the ordinary thick commercial balsam by its solubility in petroleum ether. On shaking up the carbon di-sulphide solution with a mixture of equal parts sulphuric acid and nitric acid, the latter turns brown, but the former does not assume a violet tint. When mixed with one-third volume of ammonia, a clear solution is produced. Bromine in twenty parts of chloroform gives a handsome violet coloration with the balsam. Lead acetate gives no turbidity or precipitate. The ethereal oil gives a pure red coloration with bromine-chloroform mixture, a brown-red with concentrated sulphuric acid, and a green with chloral hydrate in the warm.

10. West African (Illurin) Copaiba Balsam.

Tschirch states that a West African Copaiba balsam, obtainable in the London market, gives the same reactions as Maracaibo balsam. Umney has also examined this balsam, and is inclined to attribute it to *Hardwickia Manii*. Several kinds have also been investigated by Peinemann (*Ap. Ztg.*, 1884, pp. 8 *et seq.*), especially as regards their contained oils.

Gehe & Co. found—

Sp. gr.	0.990
Acid value, d. (S.-Z. d.) . .	57.60
Residual resin	56 per cent.

The balsam is thick, and of dark brown colour; solidifies with ammonia, but gives no colour reaction under the D. A. III. test, thus behaving like true balsams.

The author examined Illurin balsam by his own method, and found the following values:—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	58.74	59.33
Ester value (E.-Z.) . . .	9.62	9.62
Saponification value, cold (V.-Z. k.)	68.36	68.95

which agree with those obtained by Gehe & Co., and approximate Illurin balsam more nearly to Para balsam than to Maracaibo balsam.

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11. Mecca Balsam.

Balsamum de Mecca.

Origin and Habitat.—*Balsamodendron Gileadense*; *Commiphora opobalsamum*. Arabia.

Chemical Constituents.—Ethereal oil, 10 per cent.; soluble agglutinant resin, 70 per cent.; insoluble resin (burserin), 12 per cent.; bitter extract, 4 per cent.; acid matter and foreign admixtures, 1 per cent. (Bonastre); bitter principles and resenes (Baur).

General Properties and Commercial Varieties.—The balsam varies, according to age, from a pale, thin liquid

to thick, dark yellow or brown, with a very agreeable aromatic odour when fresh, but smelling of turpentine when aged.

In Bombay this Gilead balsam is known as "Balsan-Katel," and is imported from Arabia, under the name of "Duhnul-balasan." The wood of the balsam tree (*Balsamodendron opobalsamum*) is known in India by the name "Xylobalsamum," the fruit as "Carpobalsamum."

Adulterants.—Turpentine and artificial preparations of resin and oil of turpentine.

Analysis.—The published data are very scanty.

Hirschsohn found that several of the samples—of unknown purity—examined by him formed clear solutions in alcohol-ether, and also in petroleum ether.

A. Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	45·1	51·8

E. Dieterich found—

Acid value, d. (S.-Z. d.)	40·10–94·08 (!)
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Solubility in—

Ether	} complete.
Chloroform	
Acetic ether	
Benzol	
Alcohol (90 per cent.)	} almost complete.
Petroleum ether	
Oil of turpentine	
Carbon di-sulphide	

Both these authorities determined the said value by the usual method.

According to Sawyer, the pure balsam is at first turbid and white, with a strong, agreeable odour, and bitter, astringent taste. After a short time the balsam becomes thin, with a greenish sheen, then golden yellow, and finally

the colour of honey. A single drop let fall into water sinks to the bottom, then rises to the top again, where it spreads out in a cloudy film, which rapidly hardens, owing to the evaporation of the ethereal oil, and can then be taken out of the liquid. According to Guibourt, the balsam in ageing turns brown and thick, and, as a result of the volatilisation of the ethereal oil, is no longer able to reascend and spread out when dropped into water. When rubbed in the hand, the balsam loses its ethereal oil, and becomes solid. When rubbed on paper, it makes no greasy mark; and it does not harden with calcined magnesia. On mixing 5 grms. of balsam with 30 grms. of 90 per cent. alcohol, a milky liquid is produced, which in eight to ten days deposits a mucinous sediment and becomes translucent.

According to Baur, this balsam is soluble in ether, ether-alcohol, acetone, and acetic acid, but forms merely a turbid solution with alcohol, petroleum ether, benzol, chloroform, toluol, and carbon di-sulphide, a brownish yellow superficial layer separating out from the last-named solvent.

The author has applied his balsam method to several specimens of Mecca balsam, one of them (I.) being fresh, and another (II.) old and resinified. The following values were obtained :—

	I.	II.
Acid value, d. (S.-Z. d.) .	{ 39·84	60·77
	{ 39·96	61·37
Ester value (E.-Z.) .	{ 101·10	81·90
	{ 101·39	82·66
Sapon. value, cold (V.-Z. k.)	{ 140·94	142·67
	{ 141·35	144·03

The fresh, pure balsam had a very pale colour, highly agreeable aromatic odour, and lower sp. gr. than when old, the latter having a very disagreeable smell of turpentine, and being dark brown in colour and very viscid. As in the case

of copaiba balsam, the acid value increases as resinification progresses. The high acid values (up to 90) obtained by E. Dieterich probably refer to old samples.

Wiesner avers that when pure Mecca balsam is rubbed down with potato starch and examined under the microscope, the extreme outer contour of the starch granules alone remains visible, *i.e.* Mecca balsam has the same refractive power as starch. As soon, however, as an addition of fatty oil (6 per cent. and upwards) is made, the starch granules become well defined; a test enabling adulteration with such oils to be detected.

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12. Peruvian Balsam.

Balsamum de Peru (official in German Pharmacopœia).

Origin and Habitat.—*Myroxylon Pereiræ* (Papilionaceæ). Western Central America.

Chemical Constituents.—Cinnamein, consisting mainly of the benzyl ester of benzoic acid, with a smaller proportion of the benzyl ester of cinnamic acid, free cinnamic acid, vanillin, and the peruresinotannol esters of cinnamic and benzoic acids. The isolated peruresinotannol has the formula $C_{18}H_{20}O_5$ (Trog).

According to the latest researches, cinnamein is principally composed of esters of benzoic and cinnamic acids, with benzyl alcohol and a new alcohol, peruvial ($C_{13}H_{22}O$), which has an odour of honey. Cinnamic alcohol has not been detected, but di-hydrobenzoic acid is probable. The ratio of cinnamic acid to benzoic acid is about 40 : 60. Iso- and allo-cinnamic acid were not detected (Thoms).

The composition of *white* Peruvian balsam has not yet been accurately determined, the samples to be found in existing collections differing considerably from one another, so that no precise conclusions can be drawn. At all events, according to Germann, the product obtained from the fruit of *Myroxylon Pereiræ* differs in composition from the white Peruvian balsam examined by him. Guibourt classes the white (Indian) balsam as identical with the American storax from *Liquidamber styraciflua*. (See Storax.)

General Properties and Commercial Varieties.—At the present time the white variety from the fruit of *Myroxylon Pereiræ* is no longer met with in commerce, the *black* balsam alone being now listed. This latter kind forms a thick, brownish black balsam, transparent in thin layers, the odour of which is very agreeable and aromatic, and the flavour irritating. It is almost completely soluble in alcohol, chloroform, and acetic ether, but only partly soluble in other inert solvents.

The balsam recovered by boiling the bark, Balsamo de Cascara or Tacuasonte, is of inferior quality. A balsam similar to the officinal preparation, and derived from *Myrocarpus frondosus*, is no longer in commerce.

Adulterants, etc.—Ricinus oil, olive oil, and fatty oils generally, copaiba balsam, Gurjun balsam, colophony, turpentine, and Tolu balsam.

Analysis.—Like copaiba, Peruvian balsam has been widely and thoroughly investigated. Unfortunately all the trouble taken has proved unavailing, the author having shown by means of sundry samples of undoubtedly pure balsam from Honduras, taken direct from the parent tree, that all the commercial qualities of Peruvian balsam are adulterated, and that quantitative tests alone are capable of determining the value of this balsam, qualitative tests never. This explains the extraordinary divergence in the reports furnished

by various workers, each of whom had different samples of the balsam, all adulterated, as the subject of their qualitative tests.

Recently, specimens of San Salvador balsam, taken direct from the tree, were examined by Thoms, who characterises the quantitative method as the only accurate one. Of the authors who formerly occupied themselves in devising and applying qualitative reactions that are no longer suitable—such as the lime and petroleum ether tests, as well as those given in the German Pharmacopœia—the following may be mentioned:—Ulex, Grote, Evan, Nietzsche, Schweickert, Oberdörffer, Vulpius, Musset, Gehe & Co., Caesar & Loretz, Hirschsohn, Kinzel, Schade, Wimmel, Denner, and others.

The first quantitative method—determination of cinnamein, styracin, etc.—was published in a large and thorough treatise by Andrée. The same method was afterwards practised by Kremel, who, in addition, made determinations of the acid, ester, and saponification values. Gehe & Co. immediately evinced great foresight in rightly characterising these quantitative methods as a valuable progressive step.

The estimation of cinnamein was subsequently recommended by Kinzel, without any reference to the previously published labours of Andrée and Kremel. Thoms then raised objection to the methods given in the German Pharmacopœia for the determination of the acid, ester, and saponification values, by rightly laying emphasis on the existing excessive fluctuations. The sp. gr. was reported upon by Wimmel (extreme limits, 1.138 and 1.148; general range, 1.140–1.145), and also by Vulpius and Schlickum. Musset worked out a quantitative method, analogous to that of E. Dieterich by determining the portions soluble in benzine and alcohol; Denner communicated new cholesterin reactions

and a quantitative method based on the behaviour of the alkaline-earth compounds of the various constituents. (More recently the cholesterin reactions of the resins and their constituents have again been investigated by Tschirch.) By means of authentic unadulterated specimens of Honduras balsam the author has been able to show that the tests prescribed by the German Pharmacopœia are entirely erroneous. He finds that—

1. The perfectly pure balsam hardens with calcium hydrate, although the Pharmacopœia states that it should not harden.

2. When rubbed down with sulphuric acid and washed, the pure balsam does not furnish a hard mass—as required by the Pharmacopœia (D. A. III.)—but gives an almost greasy mass.

3. The test prescribed for the detection of Gurjun balsam (bluish green coloration after extraction with benzine and treatment with HNO_3) is in reality characteristic of the pure balsam, and therefore entirely useless for the purpose specified.

4. Carbon di-sulphide extracts from the pure balsam certain constituents which strongly colour the solvent. Hence the requirement of the German Pharmacopœia that the balsam should only slightly stain the carbon di-sulphide, and not turn the same brown, is in no way justified, nor does it furnish any conclusion as to the purity of the balsam.

Consequently the foregoing qualitative reactions are devoid of any value, and it is not astonishing that various authors experimenting with these methods have arrived at divergent results, or that increasing difficulty has been experienced in finding specimens that would pass the tests, even the most skilful adulterators having apparently failed.

In view of the variable composition of the product, it is

hardly a matter for surprise that the first values obtained by the use of quantitative tests were very irregular. Which of these values should be regarded as approximately normal was first shown by the author, with pure and unadulterated balsams, and later by Thoms with pure Salvador balsams.

The colour reactions with hydrochloric chloral hydrate, recently communicated by Mauch, for the detection of adulterants in Peruvian balsam may be mentioned without assigning them greater value than to colour reactions in general. The Mauch chloral hydrate method may well be useful for detecting ricinus oil (which is sparingly soluble in 60 per cent. chloral hydrate solution); treated in this way a balsam adulterated with 8 per cent. of ricinus oil gives a turbid mixture, whereas pure Peruvian balsam is soluble to a clear solution in five parts of a 60 per cent. solution of chloral hydrate.

Kremel was the first to determine the acid, ester, and saponification values, and the percentage and saponification value of the contained cinnamein and resin esters, the cinnamein estimation being performed by the Andrée method.

Kremel found—

		I.	II.	III.
Balsam	{ Acid value, d. (S.-Z. d.). . . .	40.4	40.4	49.4
	{ Ester value (E.-Z.)	187.8	199.2	181.1
	{ Saponification value, hot (V.-Z. h.)	228.2	239.6	230.5

		I.	II.	III.	IV.
Per cent. of Cinnamein	. .	68.75	67.53	66.65	77.53
Do. Resin esters	. .	29.94	32.31	32.95	21.58

Cinnamein	{ Acid value, d. (S.-Z. d.)	20.3	23.4	37.9	28.3
	{ Ester value (E.-Z.) .	214.7	207.0	202.0	68.5
	{ Saponification value, hot				
	{ (V.-Z. h.)	235.0	230.4	239.9	96.8

		I.	II.	III.
Resin esters	Acid value, d. (S.-Z. d.)	93.0	82.4	71.4
	Ester value (E.-Z.)	128.8	110.4	116.4
	Saponification value, hot (V.-Z. h.)	221.8	192.8	187.8

The following values were obtained, with Kremel's method, by E. Dieterich :—

Acid value, d. (S.-Z. d.)	30.80— 61.60
Ester value (E.-Z.)	159.60—223.60
Saponification value, hot (V.-Z. h.)	221.20—254.80
Sp. gr.	1.139

Solubility in—

Chloroform }
Acetic ether } complete.

Alcohol (90 per cent.)	99.74 per cent. soluble.
Ether	93.77—97.60 „ „
Benzol	94.27—98.03 „ „
Petroleum ether	66.04—67.93 „ „
Oil of turpentine	85.83—88.86 „ „
Carbon disulphide	86.16—87.66 „ „

The author made extensive researches with Peruvian balsam, and worked out the following new method for application thereto :—

(a) *Acid value, direct* (S.-Z. d.)—

One gram. of the balsam is dissolved in 200 c.c. of 96 per cent. alcohol and titrated with alcoholic $\frac{n}{10}$ potash, with phenolphthalein as indicator. The acid value is calculated by multiplying the volume of consumed alkali by 5.616.

(b) *Saponification value, cold* (V.-Z. k.)—

One gram. of the balsam is weighed into a 500 c.c. stoppered glass flask and left in contact with 50 c.c. of benzine (sp. gr. 0.700) and 50 c.c. of alcoholic $\frac{n}{2}$ potash for twenty-four hours at room temperature, the flask being kept well closed, and shaken up at frequent intervals. 300 c.c.

of water are then added, the whole shaken up to dissolve the deposited dark potash salts, and titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, with constant agitation. The volume (c.c.) of potash combined, multiplied by 28.08, gives the saponification value (cold).

(c) *Ester value (E.-Z.)*—

This is obtained by subtracting the results of (a) from those of (b).

(d) *Portion insoluble in ether*—

To determine this portion quantitatively, 1 grm. of the balsam is warmed with ether in a small beaker, and extracted on a tared filter until the ethereal filtrate ceases to exhibit colour or leave any residue when a single drop is tested by evaporation on a watch glass. The residue on the filter is dried at 100° C., weighed, and calculated in percentages.

(e) *Determination of the aromatic and volatile constituents (cinnamein, etc.)*—

The practical performance of the cinnamein estimation follows on after the preceding determination, the ethereal solution from (d) being shaken up with 20 c.c. of 2 per cent. caustic soda in a separating funnel and carefully separated, a single agitation being quite sufficient to dissolve the resin ester as well. The yellow ethereal solution is left to evaporate spontaneously, and, when no more ether can be detected, is placed in a desiccator for twelve hours. After weighing, the residue is returned to the desiccator for a further twelve hours and is then reweighed, the mean of the two results being taken as the normal.

(f) *Resin estimation*—

To determine the resin ester, the brown alkaline resin solution separated from the ethereal liquid is precipitated with dilute hydrochloric acid, filtered through a tared filter,

and washed, by means of the aspirator, in a minimum of water until the washings cease to give a reaction for chlorine. The resin, dried at 80° C. until constant, is then calculated in percentages. In addition, the ratio between the resin ester and cinnamein must be calculated.

(g) *Sp. gr. determination*—

By these means the author obtained the subjoined extreme values from various commercial balsams—

Sp. gr.	1.135–1.145
Acid value, d. (S.-Z. d.)	60.0– 80.0
Ester value (E.-Z.)	180.0–200.0
Saponification value, cold (V.-Z. k.)	240.0–270.0
Resin ester	20.0– 28.0%
Aromatic bodies (cinnamein, etc.) .	65.0– 77.0%
Portion insoluble in ether	1.5– 4.5%

In the case of authentically pure, natural Honduras balsam he found the values given below—

	I.	II.	III.
Acid value, d. (S.-Z. d.)	77.46	76.92	77.34
Ester value (E.-Z.)	165.61	137.42	137.67
Saponification value, cold (V.-Z. k.)	243.07	214.34	215.01
Aromatic bodies (cinnamein, etc.) .	71.41%	77.56%	73.63%
Resin ester	15.70%	13.18%	17.32%
Portion insoluble in ether	4.38%	4.31%	3.57%

The results of the author's researches on Peruvian balsam may be summarised in the following sentences:—

1. Saponification with alcoholic alkali under a reflux condenser; as also by the aqueous method, wherein steam is blown into the alkaline liquid; and by the hot method with benzine and alcoholic alkali, under a reflux condenser,—furnishes in all these cases results that are below the truth.

2. Saponification with benzine and alcoholic alkali by the cold process, and titration after dilution, gives a more sharply defined end reaction, and higher, more constant values; the

figures found in the case of the balsams examined being 260–270, against 218–259 as formerly given.

3. In determining the acid value direct, extreme dilution is necessary. The balsams examined gave values 68–80, agreeing with older figures.

4. Adulterants increase the acid value and reduce the cold saponification value, so that these changes indicate adulteration.

5. The ester value determined by difference varied only between 188 and 196 in the samples tested by the author, whereas earlier workers record 155–206.

6. An unduly low ester value indicates adulteration, and if it fall below 100 the presence of colophony, Tolu balsam, or benzoin may be inferred.

7. The estimation of the portion insoluble in ether is useful as a means of identification, but not in detecting adulteration. The proportion of this insoluble matter varied from 1.5 to 3 per cent. in the commercial varieties tested.

8. The percentage of cinnamein in the specimens examined ranged from 65 to 75 per cent., and the resin ester from 20 to 28 per cent., the ratio being 1 : 3 on the average. Ratios of 1 : 2 and 1 : 5 indicate considerable adulteration. In point of value, a balsam rich in cinnamein is superior to one rich in resin ester.

9. The refraction index of Peruvian balsam does not lie between 1.42 and 1.49, corresponding to the 100° scale of the butter refractometer.

10. The critical temperature of Peruvian balsam is indeterminable, and the Maumené value is useful merely as a means of identification.

The author has also applied this method to a number of adulterated samples, with the results given in the subjoined table :—

I. Acid value, direct—

Peruvian balsam adulterated with—	5%	10%	20%
Copaiba balsam	68·04	72·24	84·28
Storax	91·00	76·16	84·28
Colophony	91·00	148·96	166·32
Benzoin	92·40	116·20	167·44
Ricinus oil	113·12	118·72	130·48
Tolu balsam	140·00	148·96	166·32
Turpentine	66·64	62·60	—

II. Saponification value, cold—

Peruvian balsam adulterated with—	5%	10%	20%
Copaiba balsam	246·0	240·0	212·8
Storax	254·0	249·0	240·0
Colophony	252·0	252·0	—
Benzoin	240·8	236·6	232·0
Ricinus oil	243·6	236·6	229·6
Tolu balsam	258·0	252·0	243·0
Turpentine	252·0	235·0	212·8

III. Ester value—

Peruvian balsam adulterated with—	5%	10%	20%
Copaiba balsam	178·96	167·76	137·41
Storax	183·44	172·84	155·72
Colophony	161·00	104·04	65·68
Benzoin	148·40	120·40	61·62
Ricinus oil	130·48	117·88	99·12
Tolu balsam	118·00	103·24	77·28
Turpentine	186·35	172·40	—

IV. Cinnamein and aromatic constituents; also resin ester—

Peruvian balsam adulterated with—	Resin %	Cinnamein %	Resin %	Cinnamein %	Resin %	Cinnamein %
Copaiba balsam	24·05	65·95	27·98	63·03	31·90	60·82
Storax	17·28	72·35	18·06	73·02	19·06	73·70
Colophony	17·50	73·25	—	—	—	—
Benzoin	22·90	68·05	22·56	69·25	21·56	63·40
Ricinus oil	21·00	73·50	20·36	74·68	16·88	80·10
Tolu balsam	27·32	67·05	25·72	67·76	31·44	60·07
Turpentine	25·78	65·02	26·10	62·08	—	—
	5%		10%		20%	

V. Portion insoluble in ether—

Peruvian balsam adulterated with—	5%	10%	20%
Copaiba balsam	0.96	1.06	0.98
Storax	1.86	1.24	0.66
Colophony	1.70	1.62	1.05
Benzoin	1.12	0.82	0.56
Ricinus oil	0.54	0.92	0.52
Tolu balsam	0.56	0.50	0.28
Turpentine	0.94	0.92	0.61

From these data he concludes that—

1. Adulterants increase the acid value and depress the saponification value (cold); hence low saponification values and high acid values indicate adulteration.

2. An unduly low ester value points to adulteration, one below 100 indicating falsification with colophony, Tolu balsam, or benzoin.

The author agrees with Gehe & Co. that a Peruvian balsam should contain at least 65 per cent. of cinnamein (K. Dieterich method) and not more than 28 per cent. of resin ester, the value of the balsam being in direct proportion to the amount of cinnamein, and in inverse ratio to the quantity of resin present. The Honduras balsams contain over 70 per cent. of cinnamein. In order to avoid laying too stringent requirements on commercial grades, the author proposes 240 as the minimum saponification value (V.-Z. k.). Both Gehe & Co. and Caesar & Loretz refer to the author's method, and the results obtained therewith, as marking a further advance in the analysis of Peruvian balsam.

Gebe & Co. found—

Cinnamein content 57–60 per cent.
 Sapon. value, hot (V.-Z. h.), of same . 235–238 „

by the following method:—

About 5 grms. of Peruvian balsam were shaken up with 5 grms. of water and an equal quantity of standard caustic

soda solution, the cinnamein being then extracted by a triple agitation with 10 grms. of ether each time, expelling the solvent in the water bath, and weighing the residual cinnamein. Some time was required to expel the final traces of ether, and frequent weighings had to be made before the residue attained constant weight. The weighed residue was treated with 35–40 c.c. of alcoholic $\frac{n}{2}$ potash and about 20 c.c. of alcohol, and saponified in the water bath. The excess of alkali was titrated back with $\frac{n}{2}$ hydrochloric acid.

By this method Gehe & Co. examined a large number of commercial samples of Peruvian balsam, and reported twelve months after their first communication that the percentage of cinnamein in reliably pure balsams varies between 56.5 and 62.2 per cent., the saponification value (hot) of the cinnamein being 236–240.

Whereas the author, dreading an excessive and too ready volatilisation of the cinnamein during the evaporation of the solution, therefore avoids resorting to heat for this operation. Gehe & Co. had a different experience, and warmed the solution in an Erlenmeyer flask. The resulting values are consequently somewhat lower than those from the author's method, though the values in each case are concordant.

Finally, mention may be made of the combined method elaborated by Thoms from those of the author and Gehe & Co., because Thoms, as already stated, employed perfectly pure San Salvador balsams obtained direct from the gatherer.

Thoms found—

Sp. gr.	1.139	
Acid value, d. (S.-Z. d)	83	} (Dieterich method).
Sapon. value, cold (V.-Z. k)	264	
Insoluble in ether	3.36 per cent.	

Cinnamein.—(a) By the K. Dieterich method—with this

modification, that the ethereal solution of cinnamein was shaken up twice with 2 per cent. caustic soda, followed by shaking up twice with water, and warming the residue half an hour in the water bath after the evaporation of the ether—

1. = 60·84 per cent.
2. = 60·88 „
3. = 61·30 „

(b) By Gehe & Co.'s method—

4. = 60·52 per cent.
5. = 61·036 „
6. = 60·22 „
7. = 60·768 „

The estimations Nos. 1 and 2 were made by Lüders, No. 3 by Thoms, Nos. 4 to 7 by E. Kennert. Four of the tests were performed by the Gehe method, in order to ascertain the effect of varying durations of the evaporative process on the yield of cinnamein. The foregoing figures show that no great fluctuations were produced.

Ester value of cinnamein (Gehe's so-called "saponification value")—

(a) Of the cinnamein obtained by the Dieterich method—

No. 3. = 239·8

(b) Of the cinnamein from the Gehe method—

No. 7. = 240·9

Resin ester (Dieterich method)—

No. 1. = 20·28

No. 2. = 19·76

Thoms prefers the author's agitation method, but repeated the shaking up several times, and thereby obtained values agreeing with those of Gehe & Co.

The saponification value (V.-Z. h.), or more properly the Ester value (E.-Z.), of cinnamein, was determined by Thoms in the following manner :—

The cinnamein is washed by a little alcohol into a flask, where it is treated for an hour with 50 c.c. of alcoholic $\frac{n}{10}$ potash, and afterwards warmed in the water bath for another hour.

The precipitated potassium salt is redissolved in a little water and, when cooled, the whole is titrated back with $\frac{n}{10}$ hydrochloric acid in presence of phenolphthalein. The difference between this value and 50, multiplied by 0.005616, gives the quantity of KHO consumed in saponifying the cinnamein present.

The following results were obtained by Hampe in applying the author's method to an adulterated sample of Peruvian balsam :—

Acid value, d. (S.-Z. d.)	72.90–74.09
Ester value (E.-Z.).	145.01–145.04 (!)
Saponification value, cold (V.-Z. k.)	218.3 –219.1 (!)
Insoluble in ether	0.93 per cent. (!)
Cinnamein and aromatic constituents	58.69 „ (!)
Resin ester	24.28 „ (!)

The sample did not form a perfectly clear solution in 60 per cent. chloral hydrate. It was very thin, and rather pale in colour, reddish in thin layers.

Since the values given by normal balsam lie within other limits, the saponification value being not less than 140, the insoluble in ether not below 1.5 per cent., and the cinnamein content not lower than 65 per cent., the foregoing balsam was undoubtedly adulterated.

The author found in his researches on Peruvian balsam (*H. A.*, 1896) that adulterants raise the acid and lower the saponification values. Perfectly pure balsams contain up to 4 per cent. of matters insoluble in ether, and form a perfectly clear and complete solution in the aforesaid chloral hydrate solvent. From these results, it is evident that the author's method answers well in practice.

The following values were obtained by Gregor as methoxyl values (M.-Z.):—

16·7

21·8

22·6

With regard to the German Pharmacopœia tests for Peruvian balsam, the reader is referred to the author's paper in the *Ph. C.*, 1898, No. 19.

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13. Tolu Balsam.

Balsamum de Tolu (officinal in German Pharmacopœia III.).

Origin and Habitat.—*Myroxylon Toluifera* (Papilionaceæ). Northern portion of South America.

Chemical Constituents.—Acids, oily constituents mainly composed of the benzyl ester of benzoic acid, and to a smaller extent of the benzyl ester of cinnamic acid, 7·5 per cent.; impurities, 3 per cent.; vanillin, 0·05 per cent.; cinnamic and benzoic acids, 12-15 per cent.; the tolu-

resinotannol esters of cinammic and benzoic acids. According to Oberländer, the isolated toluresinotannol has the formula $C_{16}H_{14}O_3OCH_3OH$.

General Properties and Commercial Varieties.—When fresh, the balsam is brownish yellow, quite transparent in thin layers, and free from crystals. Older specimens are hardened, and exhibit a crystalline structure under the microscope; the colour is reddish brown; melting-point, 60° – 65° C.; flavour, aromatic and irritant. It is soluble in alcohol, chloroform, and alkalis, the alcoholic solution having an acid reaction. The opinion that carbon di-sulphide does not dissolve this balsam (see Detection of Colophony) is untenable, samples being known which give up considerable amounts to this solvent.

Adulterant.—Colophony.

Analysis.—Earlier examinations of Tolu balsam showed that this product is largely adulterated, mostly with colophony. The practice had been largely promoted by the remarkable requirements laid down by the German Pharmacopœia (D. A. III.), which prescribes “hardened” balsam. The values obtained must therefore be accepted with a certain amount of reserve. The qualitative detection of colophony has been dealt with by Braithwaite, Gehe & Co., Cripps, and Hirschsohn, whilst Thoms and Gehe & Co. have criticised the German Pharmacopœia tests. Particulars of the Storch-Morawski method for detecting colophony will be found in the description, etc., of that resin. Another point recommended as a special criterion of Tolu balsam, was the degree of solubility in benzol (maximum, 5 per cent.). Quantitative researches, dealing particularly with the determination of the acid, ester, and saponification values, by the usual methods, were first published by Kremel, and afterwards by Beckurts and Brüche.

A. Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	127.2	100.6
Ester value (E.-Z)	26.7	58.7
Saponification value, hot (V.-Z. h.)	153.9	159.3

Beckurts and Brüche found—

Sp. gr.	1.092–1.101
Acid value, d. (S.-Z. d.)	106–132
Ester value (E.-Z.)	55– 71
Saponification value, hot (V.-Z. h.)	177–188
Ash	0.25–1.2 %

They preferred the Schmidt test to the acid value determination as a means of detecting colophony, since the acid value does not begin to work out abnormally high until the proportion of colophony attains 20 per cent. In the Schmidt test, 0.5 grm. of balsam is left in contact with 25 c.c. of carbon di-sulphide for half an hour, with occasional shaking; then filtered, and the filtrate evaporated in a porcelain basin. Colophony, when present, is revealed in the residue by its smell and the green coloration produced on adding a few drops of sulphuric acid to the dissolved residue. Pure Tolu balsam should be practically insoluble in carbon di-sulphide. According to Braithwaite, however, this solvent removes cinnamic acid; and this authority prescribed the following modification of the above test:—When 5 parts of the balsam are warmed twice with 25 or 10 parts of carbon di-sulphide, the filtrate should leave, on evaporation, a crystalline residue, which should give a (hot) saponification value of not less than 300 parts KHO per 1000 parts.

Schmidt's results conflicted greatly with those of E. Dieterich (see below), who found nearly 90 per cent. soluble in carbon di-sulphide; and, in any event, this portion of the Schmidt test is uncertain.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	114·80–158·60
Ester value (E.-Z.)	31·20– 40·50
Saponification value, hot (V.-Z. h.) . .	155·30–187·40

Solubility in—

Alcohol (90 per cent.)	} complete.
Acetic ether	

Chloroform—almost complete.

Ether 53·20–87·90 % soluble.

Benzol 82·27 % to almost complete.

Petroleum ether	2·22–10·22 %	} soluble.
Oil of turpentine	27·82–54·55 %	
Carbon di-sulphide	19·60–88·18 %	

These very high rates of solubility in carbon di-sulphide show the unreliability of this portion of the Schmidt test, although it may be presumed that adulterated samples were employed. At any rate, the acid, ester, and saponification values afford a better criterion. Pure Tolu balsam appears to be practically unknown in commerce, a circumstance explaining the small reliance to be placed on the above test. A renewed thorough investigation of this product is urgently required.

With regard to the testing and solubility of Tolu balsam, Gehe & Co. express themselves as follows:—

Under prolonged storage, or as the result of a brief warming in the water bath, the balsam loses 8–10 per cent. in weight, and passes into a brittle condition. The preference given in the Pharmacopœia to hardened balsam, for which tenable grounds are lacking, is the reason why the hard balsams now current in the German drug market are almost exclusively hardened with colophony, which cannot be detected by the test prescribed in the Pharmacopœia. Even pure balsam is not insoluble in carbon

di-sulphide, but gives up as much as 25 per cent. to that solvent. Others even state that some kinds are soluble up to 80 per cent., though the purity of such samples appears to us questionable.

The foregoing opinion agrees with the author's views on the tests and prescriptions of the German Pharmacopœia, and on the carbon di-sulphide test.

The values obtained with the author coincide fairly with those recorded by Beckurts and Brüche, Kremel, and E. Dieterich, and therefore do not need to be cited here. Tolu balsam should contain as little ash as possible.

The methoxyl value (M.-Z.) is given by Gregor as 41.6–41.7, and by Bamberger as 46.8.

The German Pharmacopœia test for Tolu balsam was discussed by the author in the *Ph. C.*, 1898, No. 19.

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B. RESINS.

BEFORE dealing with the resins separately, it may be premised that for this group of substances, just as with the gum resins, much more divergent methods have been employed for determining their characteristic constants than is the case with the balsams. Extracts have been used to some extent which no longer corresponded to the natural drugs; which is sufficient to partly explain the great fluctuations observable in the results, though these are also in some degree attributable to the very dark solutions given by the (mostly coloured) resins.

A series of uniform methods, based on the modern chemistry of resins, tested in practice, and capable of obviating similar inconveniences, was recently made public by the author; and it is highly desirable that contributions to the establishment of a uniform system of judging, on a modern basis, should be presented by other workers, or that existing data should be subjected to confirmation, in order to furnish the highly necessary accumulation of numerical details.

14. Acaroid Resin.

Resina Acaroïdes (Xanthorrhæa Resin).

I. RED ACAROID RESIN.

Origin and Habitat.—*Xanthorrhæa Australis*, *X. quadrangularis*, *X. Drummondii*, *X. Preisii*, etc., chiefly different species of *Xanthorrhæa* (Asphodeleæ). New South Wales.

Chemical Constituents.—Paracumaric acid, $C_9H_8O_3$, in a

free state (1 per cent.); benzoic acid (traces) and paracumaric acid (2 per cent.), both in combination with erythroresinotannol, $C_{40}H_{39}O_9OH$; paraoxybenzaldehyde (0·6 per cent.). The bulk (85 per cent.) of the resin consists of the erythroresinotannol ester of paracumaric acid. According to Hildebrand, the absence of cinnamic acid distinguishes this resin from yellow acaroid.

II. YELLOW ACAROID RESIN.

Origin and Habitat.—*Xanthorrhoea hastilis* (Asphodeleæ). Tasmania.

Chemical Constituents.—Free paracumaric acid ($C_9H_8O_3$), 4 per cent.; free cinnamic acid, 0·5 per cent.; combined paracumaric acid, 7 per cent.; combined cinnamic acid, 0·6 per cent. Both acids form esters with xanthoresinotannol ($C_{43}H_{45}O_9OH$), producing chiefly the corresponding ester of paracumaric acid, which forms the main constituent of this resin. In addition, there are also present styracin ($C_{18}H_{16}O_2$), cinnamic phenylpropyl ester (?), paraoxybenzaldehyde (?), and vanillin (?), the latter, however, being somewhat uncertain. (Hildebrand.)

General Properties and Commercial Varieties.—The *red resin*, or “grass tree gum,” forms small, red-brown, dusty lumps, with lustrous fracture, and about 10 per cent. of impurities; it is completely soluble in alcohol, and gives no reaction for cinnamic acid.

The *yellow resin* (*Resina lutea*, Botany Bay gum) is of a transparent yellow colour, also dusty, and gives the cinnamic acid reaction.

Australian acaroid resins are now being collected, and are justly recommended as substitutes for colophony, particularly for sizing paper, for which purpose they have long been used in North America, as well as for enriching gas, and in

the manufacture of varnishes and perfumery ware. The resins of the various *Xanthorrhœa* species differ not inconsiderably both externally and inwardly. (K. Dieterich, *H. A.*, 1897, pp. 37, 38.)

Adulterants, etc.—Owing to the relatively low price of these resins, the only impurities likely to occur are extraneous mineral and vegetable matters. The different qualities of acaroid resin are also liable to be mistaken one for another.

Analysis.—Although actual analytical reports on the acaroid resins are practically non-existent, this technically important material has been mentioned here on account of its introduction into Europe, and employment in the preparation of varnishes, paper, and perfumery. Its application to the production of gas is worthy of mention; and in America it is used medicinally as a tincture (60 grms. of resin per litre of alcohol) in doses up to 70 grms. for phthisis and chronic catarrh. At the present time, acaroid resin from *X. quadrangularis* is obtainable at a low price from Australia, and has rightly found favour.

According to Maiden, the yellow acaroid resin does not soften in the mouth. Petroleum ether dissolves 1–2 per cent., and alcohol, 91–94 per cent. According to the author's researches, the acaroid resin from *X. quadrangularis*, and other red varieties, resembles the yellow resin in containing no cinnamic acid.

The red resin from *X. arborea* is soluble to the extent of about 3 per cent. in petroleum ether, but dissolves entirely in alcohol, except for the 5–10 per cent. of contained impurities. Hirschsohn found three different kinds to be completely soluble in alcohol, but only imperfectly so in chloroform and ether.

Proper analytical data are very scarce. Schimmel & Co. report the following values for yellow acaroid resin oil:—

Acid value, d. (S.-Z. d.), 4.9; ester value (E.-Z.), 69.4; and saponification value, hot (V.-Z. h.), 74.3. This oil is practically unimportant.

Kitt found the following carbonyl values:—

Yellow acaroid resin	0.29–0.46
Red do.	0.84–0.98

On the worth of these values, the author expressed himself in *Chem. Rev.*, 1898, No. 10 (see also Wiesner, *Die technisch verwendeten Gummiarten, Balsame, und Harze*, pp. 189–195). In view of the important technical future before the acaroid resins, further analytical data are highly desirable.

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15. Anime.

Resina Anime.

Origin and Habitat.—The source of this resin is very uncertain, there being a number of other closely allied kinds, such as eleme, *Resina kikekunemalo*, *Resina tacamahaca* (*q.v.*). In England the name “anime” is applied to copal, the soft varieties in particular, and some French drug merchants call Madagascar copal, “animé.” The resin from *Hymenaea Courbaril* is an entirely different product to West or East Indian anime, and the reason that anime has been erroneously confounded with Courbaril resin (Schmidt’s *Organ. Chemie*, 1896; Kolbe’s *Organ. Chemie*, 1868), and *H. Courbaril* regarded as the source of anime, is because Courbaril resin is called “American copal,” and, as a soft copal, is termed “anime” in England. Even a superficial examination of

anime resin and its odour will be sufficient to clearly show that it has nothing in common with Courbaril and Madagascar copals. Anime is more nearly allied to elemi, whilst Courbaril and Madagascar are nearer to true copal. Probably, like elemi, anime is obtained from a species of *Icica* (*Burseraceæ*). West and East Indies.

Chemical Constituents.—Resin soluble in cold alcohol, 54·30 per cent.; pale yellow gelatinous sub-resin, resembling turpentine in appearance, insoluble in cold, but soluble in hot, alcohol, 42·80 per cent.; ethereal oil, 24 per cent. (Paoli).

General Properties and Commercial Varieties.—*West Indian anime* is in the form of brittle lumps, covered outside with white dust, yellowish white in colour internally, with a slight resinous lustre, smelling more like elemi than incense, and softening like mastic when chewed. It is almost completely soluble in hot alcohol, but only imperfectly so in cold alcohol or benzine. This variety is darker than that from the East Indies.

East Indian anime takes the form of masses composed of smaller, rounded, irregular granules, of uneven reddish yellow colour, which are brittle and of waxy, lustrous fracture. It is more difficult to soften than the above variety, and is lighter coloured and stronger smelling—the odour resembling that of dill and fennel.

Adulterants, etc.—Vegetable and mineral substances.

Analysis.—No pure or characteristic specimens of this product being any more met with in commerce, the practical absence of analytical data is not surprising. Within the last decade anime was still an article of trade, but has now almost entirely disappeared. Williams examined several kinds of the natural product, by the usual methods, and obtained the following values:—

	I.	II.	III.
Acid value, d. (S.-Z. d.) .	26·6	18·2	25·2
Ester value (E.-Z.) . .	47·0	55·4	62·3
Sapon. value, hot (V.-Z. h.)	73·6	73·6	87·5
Moisture	0·1%	0·48%	0·31%
Ash	0·05%	0·11%	0·07%

Hirschsohn obtained the following values for the (dried) constituents soluble in petroleum ether at 120° C.:—

Anime occidentale . . .	72·89 per cent. soluble.
Do. orientale . . .	74·05 „ „
Do. do. . . .	65·05 „ „
Do. do. . . .	77·85 „ „

The author has examined East and West Indian anime by the same methods as Williams, and found the values given below:—

	East Indian.		West Indian.	
	I.	II.	III.	IV.
Acid value, d. (S.-Z. d.) .	29·69	30·64	45·36	47·20
Ester value (E.-Z.) . .	29·77	38·76	113·93	102·39
Sapon. value, hot (V.-Z. h)	59·46	69·31	159·29	149·59

The figures for I. and II. agree closely with those found by Williams, so that possibly the specimens examined by that worker were also East Indian anime. The values for the West Indian variety are seemingly much higher than those furnished by East Indian anime.

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16. Amber.¹

Succinum, Succinite.

Origin and Habitat.—*Pinites succifer* (primeval) (*Abietinæ*). Prussian Baltic coast.

¹ The collective term "amber," which comprises a number of fossil resins, such as Succinite, Glessite, Stantienite, Beckerite, etc., is restricted here to Succinite, or true amber.

Chemical Constituents.—The borneol ester of succinoabietic acid, 2 per cent.; free succinoabietic acid ($C_{80}H_{120}O_5$), 28 per cent.; succinic succinoresinol ester ($C_{12}H_{20}O$), 70 per cent. When split up by alcoholic caustic potash, succinoabietic acid yields a divalent alcohol. Succinoabietol ($C_{40}H_{60}O_2$) and succinosilvic acid ($C_{24}H_{36}O_2$). Succinic succinoresinol ester is an oxidation product of succinoabietic acid. The portion of succinite insoluble in alcohol consists entirely of the succinic ester of succinoresinol. According to Aweng succinite contains sulphur.

Gedanite has the same constituents as succinite, except that sulphur is absent. Owing to its inferior hardness as compared with succinite, Helm termed this variety "friable amber." *Glessite* seems to agree with succinite in composition, except that, instead of borneol, it contains a substance recalling carvol. *Allingite* contains sulphur, but neither borneol nor succinic acid; and, according to Aweng, the resin acid it yields is not identical with succinic acid.

General Properties and Commercial Varieties.—*Succinite*: yellow or yellowish brown, translucent or opaque, brittle lumps, with lustrous conchoid fracture; melting-point, 250° – 300° C.

Gedanite is of whitish yellow colour and transparent, without fluorescence or polarisation; readily fractured; froths up at 140° and 180° C.

Glessite when examined under the microscope (100 diameters) exhibits a cellular, globular structure, with granular contents. It has the same m.p. as succinite.

Allingite is whitish yellow to reddish in colour, melts at 300° C., and is of sp. gr. 1.076.

Amber-guaiacum resin is not an amber, but a good quality of guaiacum (*q.v.*). The amber from the Baltic coast is specially known as Baltic amber.

Adulterants, etc.—Copal, colophony, and artificial amber.

Analysis.—The present is not a suitable occasion for discussing more closely the many valuable contributions made by O. Helm,¹ or for reporting all the properties of the various kinds of amber mentioned above. A few important data that may be useful to the analyst in the differentiation of the various grades are subjoined from the publications of Helm and Potonié.² According to the latter, the following varieties of amber should be regarded as distinct:—

I. *Gedanite*: pure yellow, transparent, frothing up at 140°–180°C. and melting when heated further; also called “friable amber,” and contains less succinic acid than succinite.

II. *Glessite*: usually brown and opaque.

III. *Stantienite*, or “black resin”: very brittle and pulverulent.

IV. *Beckerite*, or “brown resin”: opaque and viscous.

V. *Succinite*, or “true amber”: sp. gr. 1·050–1·096, m.p. 250°–300°C.

In working up amber into varnish, it is melted or distilled (compare copal and dammar), the amber oil being then used as a solvent. When melted or distilled, amber is more readily soluble in oil of turpentine and fatty oils than in the crude state.

(For a description of Silician and Roumanian amber, see O. Helm, *A. d. Ph.* 218, pp. 307, 447.)

It should be stated that amber is liable to be confounded with copal, which is employed to adulterate it, and that they may be differentiated by the fact that amber is insoluble in cajeput oil, which completely dissolves copal (*q.v.*).

¹ Particularly *A. d. Ph.* 213, 215, and 222.

² *Ph. C.*, 1890, p. 744.

According to Flemming, both copal and amber are soluble in the chlorhydrins of glycerin (epi-dichlorhydrin)—see table pp. 25 to 27; and true copal (not copal from *Dipterocarpeæ* and *Coniferae*!—see Copal) is practically insoluble in 60 per cent. chloral hydrate. Furthermore, copal gives no ester value, whereas amber does; and, in addition, copal is characterised by its ready solubility in ether and cajeput oil, as well as by the negative results furnished by testing a burning sample with paper moistened with lead acetate (absence of sulphurous bodies which escape from heated amber as secondary compounds and stain the test paper black). Amber is artificially imitated by coloured glass, celluloid, or colophony with artificial adjuncts. To detect colophony it is merely necessary to drop a little alcohol or ethylsulphuric acid on the suspected sample; pure amber is unattacked by these reagents, whereas an impure specimen will show a dull spot. The melting-point also affords a definite indication of purity.

Since it may happen that a large block of amber has been artificially prepared by pressing together a number of small fragments of amber, so that, by this means, inferior waste is worked up into valuable large lumps, O. Helm devised a method for detecting such artificial products. With regard to “imitation amber” he says—

“When polished, the transparent pressed blocks exhibit a peculiarity distinguishable by none but a skilled eye, namely, when the block is held up to the light, so far from its structure being perfectly homogeneous, the whole interior seems to be traversed by a number of hazy wave-like films, which are in reality the surfaces of contact of the individual lumps composing the block.

“Under polarised light this pressed amber behaves in a very characteristic manner. When placed between crossed Nicol prisms, polished Baltic amber reveals faint, but seldom

bright, interference bands. On rotating the polariscope through 90° the colours pass into their complementaries, and return to their original condition when the rotation attains 180° , thus changing twice during a complete revolution. The usual colours observed are red, green, and orange, to blue. A block composed of small fragments of amber pressed together always exhibits bright interference bands, both adjacent and frequently intermixed, which vary according to the size of the constituent fragments, on changing the field of vision. Frequently all shades of colour can be seen in the field at once, and change into their complementaries on the polariscope being rotated through 90° ."

In the less transparent kinds of amber this means of differentiation is not so readily applicable. Klebs, however, has found another characteristic indication. As already observed by Helm, in 1878, all cloudy and opaque kinds of amber, when viewed under the microscope, exhibit in their interior a number of round, oval, or elongated cavities of various dimensions. The size, position, and number of these cavities differ greatly, and give rise to the different qualities of commercial clouded amber. Under the heavy pressure (up to 3000 atmos.) employed in making the artificial blocks, these cavities are compressed, and, when viewed under the microscope, exhibit a flattened, often dendritic appearance. In addition, it is stated by Klebs that clouded pressed amber can be recognised by the more cloudy appearance of the clear matrix, the turbid portions being seemingly arranged in parallel strips, like cirrus clouds. At the planes of transition between the clear and clouded parts, the yellowish red tinge produced by transmitted light and the bluish sheen by reflected light (with dark background) are thrown up more distinctly by the extremely fine cavities than is the case with natural amber.

O. Rössler reports as follows on the differentiation between copal and amber:—

“To decide whether a sample is true amber or a fossilised East African copal, the sulphur content should be examined. When a fragment of amber is heated in a small glass tube, fused at the lower end, sulphurous vapours are evolved, and will blacken a piece of paper, moistened with lead acetate, held at the mouth. On the other hand the copals, of whatever origin, are free from sulphur. Samples of amber from Troy and Mycene were found to be true amber.”

In addition to the differential characteristics of the various kinds, and the adulterations, a number of purely analytical data are available.

Thus Williams found—

Acid value, d. (S.-Z. d.)	15·4
Ester value (E.-Z)	71·4
Saponification value, hot (V.-Z. h.)	86·8
Moisture	1·05 per cent.
Ash	0·28 „

by the usual methods.

A. Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	34·4	33·4
Ester value (E.-Z.)	74·5	91·1
Saponification value, hot (V.-Z. h.)	108·9	124·5

by the same methods; the concordance is not very striking.

Von Schmidt and Erban found—

Natural amber—Saponification value, hot	144·8
Fused amber—Saponification value, hot	36·0

values which, although determined by the same methods as used by the earlier authors, agree but poorly with the latter's results. In point of solubility, von Schmidt and Erban give the following particulars:—

Solubility in—	Fused.	Natural.
Alcohol . . .	almost insoluble	almost insoluble.
Ether . . .	partly soluble	almost insoluble.
Methyl alcohol . .	almost insoluble	almost insoluble.
Amyl alcohol . .	partly soluble	almost insoluble.
Benzol . . .	almost entirely soluble	almost insoluble.
Petroleum ether . .	almost insoluble	almost insoluble.
Acetone . . .	almost insoluble	insoluble.
Glacial acetic acid .	partly soluble	almost insoluble.
Chloroform . . .	partly soluble	almost insoluble.
Carbon di-sulphide .	almost entirely soluble	partly soluble.
Oil of turpentine . .	almost entirely soluble	partly soluble.

As already mentioned, amber, being an esteriferous resin, gives ester values, and is thus analytically distinguishable from copal, which does not.

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17. Siam Benzoin.

Resina Benzoës (officinal in German Pharmacopœia).

Origin and Habitat.—*Styrax Benzoin* (Styracæ). Siam.

Chemical Constituents.—Oily neutral liquid, an ester of benzoic acid (the alcohol being probably cinnamic or benzyl alcohol), 0·3 per cent.; vanillin, 0·15 per cent.; free benzoic acid; impurities, 1·6–3·3 per cent.; benzoic benzoiresinol ester, and benzoic siaresinotannol ester. Benzoiresinol has the formula $C_{16}H_{26}O_2$; siaresinotannol, the formula $C_{12}H_{14}O_3$. The bulk of Siam benzoin consists of the mixture of benzoic benzoiresinol ester and benzoic siaresinotannol ester:—

Benzoic acid . . .	38·2 per cent.	
Siaresinotannol . .	56·7	„
Benzoiresinol . . .	5·1	„ (Lüdy).

General Properties and Commercial Varieties.—

Whilst *Siam benzoin* is in the form of smooth, rounded, brownish lumps, white inside and generally light coloured and pure, the other varieties—such as *Sumatra*, *Padang*, *Penang*, and *Palembang* benzoin—are impure blocks or masses of a reddish grey colour, with isolated embedded pale tears. Siam, Padang, and Palembang benzoin contain no cinnamic acid, which, however, is present in the Sumatra and Penang varieties. Siam benzoin is the best kind, Palembang and Sumatra coming next in order.

Adulterants, etc.—Siam benzoin is adulterated with Padang and Palembang benzoin, and with mechanical impurities; Sumatra benzoin, with Palembang, and mechanical impurities, colophony, dammar, storax, and turpentine.

Analysis.—A number of authors, among whom may be mentioned Stoltze, Grassmann, Helmstädt, Frémy, v. d. Pliet, Wach, Unverdorben, Kopp, Hirschsohn, etc., have examined the various benzoin, more especially for their solubility, ash content, adulterants, and so on. For the most part the distinctive tests applied were merely qualitative; a very thorough paper published some years ago in the *A. d. Ph.* (200, p. 205) deserves mention on account of its comprehensive character. Subsequently Hirschsohn examined the various kinds with regard to their percentage content of substances soluble in petroleum ether; and then quantitative determinations were made by Kremel, Schmidt and Erban, Beckurts and Brüche, Helbing, Lüdy, E. Dieterich, Evans, Dunlop, K. Dieterich, and others. Fr. Lüdy, to whom we are indebted for an accurate knowledge of the different kinds of benzoin, and who has examined them on the basis of modern resin chemistry, must be considered as an experienced connoisseur of these bodies. He states that the very fluctuating values obtained are attributable to the lack of uniform

methods. Unfortunately no one else but the author appears to have investigated pure and adulterated benzoin on the lines of more recent experience. According to Lüdy, Siam and Palembang benzoin differ from Sumatra and Penang benzoin by the fact that the former contain benzoic acid and the latter cinnamic acid. It may also be mentioned that the author has reported obtaining the reactions of cinnamic acid with a Siam benzoin from the London market; so that Siam benzoin containing cinnamic acid would appear to exist, even though rarely met with. Helbing has shown that benzoin is largely adulterated, in the artificial products, containing sand, resin, and tale, which he obtained in the London Docks.

Hirschsohn found—

		Per cent. soluble in Petroleum Ether—	
		at 17° C.	120° C. dried.
Siam benzoin	. . .	27.53	16.49
Do.	. . .	26.66	21.19
Do.	in grains .	28.73	17.49

The acid, ether, saponification, and methoxyl values have also been determined. The figures quoted by Williams cannot be taken into consideration, the variety of benzoin being left unspecified. For the sake of completeness mention is made of the colour reactions obtained by Mauch with benzoin and chloral hydrate, without crediting them with more value than colour reactions in general. Von Schmidt and Erban have also reported on the solubility, acid value, and saponification value of benzoin, but without giving the name of the variety examined. The detection of colophony in benzoin by the Storch-Morawski reaction will be found under "Colophony."

A. Kremel found, from an extract—

Acid value, d. (S.-Z. d.)	. . .	141.1
Ester value (E.-Z.)	. . .	55.4
Saponification value, hot (V.-Z. h.)	.	196.5

but as the natural drug was not employed these figures have a merely relative value.

Beckurts and Brüche found—

	Sp. gr.	1.150–1.171
	Ash	0.27–1.04 per cent.
	Insoluble in alcohol	2.1–4.0 „
From extract	{ Acid value, d. (S.-Z. d.)	119–167
	{ Ester value (E.-Z.)	39– 60
	{ Saponification value, hot (V.-Z. h.)	172–211

The same remark applies to these last three values as to those of Kremel and the following:—

E. Dieterich found—

From an extract	{ Acid value, d. (S.-Z. d.)	140.0
	{ Ester value (E.-Z.)	35.0
	{ Saponification value, hot (V.-Z. h.)	175.0

All the foregoing authors worked with extracts, and by the usual methods.

Evans found 1.30–2.48 per cent. of matters insoluble in alcohol.

The author has recently made a thorough examination of the various benzoin, and has elaborated the following methods for dealing with the natural drugs instead of extracts:—

I. *Determination of ash.*

II. *Acid value, ind.* (S.-Z. ind.).

One grm. of Siam benzoin, taken from a large average sample of the finely powdered drug, is treated in a flask with 10 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of 96 per cent. alcohol for exactly five minutes, and then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein until a single drop of the indicator no longer assumes a red coloration when introduced, and until the precipitated salts rapidly and completely subside. The supernatant liquid should be of a pure yellow colour. The volume (c.c.) of combined alkali multiplied by 28.08 gives the indirect acid value (S.-Z. ind.).

III. *Saponification value, cold* (V.-Z. k.).

One grm. of Siam benzoin taken, as before, from an average sample, is placed in a stoppered flask, and suffused with 20 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0.700). After leaving the closed flask for twenty-four hours at room temperature, the contents are diluted with alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The number of c.c. of combined KHO multiplied by 28.08 gives the cold saponification value.

IV. The *ester value* is found by subtracting the above acid value from the saponification value.

The following constants, etc., are given as characteristic of Siam benzoin, examined by the author's method:—

- I. Ash = 0.03–1.50 per cent.
 - II. Solubility in alcohol should be complete except for a minute vegetable residue, 5 per cent. being the highest permissible limit.
 - III. Acid value, ind. (S.-Z. ind.) = 140–170
 - IV. Ester value (E.-Z.) = 50–75
 - V. Saponification value, cold (V.-Z. k.) = 220–240
- } by above method.

The author examined the influence of various adulterants, *e.g.* colophony, dammar, storax, and turpentine, on these normal values, with the result that dammar was found to depress the acid value, turpentine the ester and saponification values, and storax the acid value; colophony, however, being difficult to detect, and only when present in large quantities. The melting-point and solubility in alcohol will also afford useful aid in this connection.

Finally, it may be mentioned that the following methoxyl values were obtained from Siam benzoin by Gregor and Bamberger:—

	Gregor.	Bamberger.
Methoxyl value . . .	43.4	30.0
Do.	43.0	28.5

(As to the worth of these figures compare *Chem. Rev.*, 1898, No. 10; and on the German Pharmacopœia tests for Siam benzoïn, see *Ph. C.*, 1898, No. 20.)

18. Sumatra Benzoïn.

Origin and Habitat.—*Styrac Benzoin* (Styracææ). Sumatra.

Chemical Constituents.—Ash, 0·01 per cent.; free benzoic acid; styrol; traces of benzaldehyde (C_6H_5COH); benzol (C_6H_6); vanillin ($C_8H_8O_3$), 1 per cent.; cinnamic phenylpropyl ester ($C_{18}H_{18}O_2$), about 1 per cent.; cinnamocinnamic ester = styracin ($C_{18}H_{19}O_4C_9H_7O$), about 2–3 per cent.; cinnamic benzoiresinol ester ($C_{16}H_{25}O_2C_9H_7O$), and cinnamic benzoiresinotannol ester,—this ester mixture is the main component of Sumatra benzoïn. The isolated alcohols have the formulæ—benzoiresinol (crystalline) = $C_{16}H_{26}O_2$, and benzoiresinotannol (amorphous) = $C_{18}H_{20}O_4$. The impurities amount to about 14–17 per cent. (Fr. Lüdy.)

General Properties and Commercial Varieties.—See Siam benzoïn, as also for **Adulterants**.

Analysis:—

Hirschsohn found—

	Per cent. soluble in Petroleum Ether—	
	Dried at 17° C.	at 120° C.
Sumatra benzoïn . . .	12·06	4·48
Do.	7·70	2·06
Do.	4·90	3·64
Do.	9·83	2·98

A. Kremel found (from extract)—

Acid value, d. (S.-Z. d.)	96·0
Ester value (E.-Z.)	60·9
Saponification value, hot (V.-Z. h.)	156·9

As in the case of Siam benzoin (*q.v.*) these figures are only of relative value.

Beckurts and Brüche found—

	Sp. gr.	1.120–1.154
	Ash	0.15–0.60 %
	Insoluble in alcohol	6–7 %
From extract	{ Acid value, d. (S.-Z. d.)	97–132
	{ Ester value (E.-Z.)	48–65
	{ Saponification value, hot (V.-Z. h.)	160–188

These last three values, like those found by Kremel, having been obtained from extracts, are not to be relied on as representing the natural product.

E. Dieterich found—

From extract	{ Acid value, d. (S.-Z. d.)	93.76–186.60
	{ Ester value (E.-Z.)	29.40–170.80
	{ Saponification value hot (V.-Z. h.)	160.64–265.05
	Moisture	4.00– 8.20
	Ash	0.57– 1.23 %
	Soluble in 96 per cent. alcohol	68.09– 85.80 %

The above remarks apply also to the first three values on this list.

The author has elaborated the following new method for Sumatra benzoin :—

(a) *Acid value, ind.* (S.-Z. ind.).

One grm. of benzoin, taken from a large finely powdered average sample of the drug, is placed in a flask and treated with 10 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of 96 per cent. alcohol. After leaving for exactly five minutes—no more—the contents are titrated back until yellow, with $\frac{n}{2}$ sulphuric acid and phenolphthalein, *i.e.* until an added drop of the indicator no longer turns red, and until the precipitated salts settle down quickly and completely. The supernatant liquid should be pure yellow in colour. The acid value is

found by multiplying the number of c.c. of combined KHO by 28·08.

(b) *Saponification value, cold* (V.-Z. k.).

One grm. of benzoin is taken from an average sample as before, placed in a stoppered flask holding 1 litre, and suffused with 20 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0·700). After standing for twenty-four hours at room temperature, the contents are diluted with alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The saponification value is found by multiplying the volume (c.c.) of combined KHO by 28·08.

(c) *Ester value* (E.-Z.) obtained by subtracting the above acid value from the saponification value.

(d) *Matters soluble in alcohol.*

Ten grms. of benzoin are extracted with hot 96 per cent. alcohol, the solution being then evaporated, and the residue dried at 100° C. and weighed. The undissolved portion is collected on a filter, and estimated after drying at 100° C.

(e) *Ash*.—One grm. of substance is incinerated and calcined until of constant weight.

By this method the author obtained the following values :—

Acid value, ind. (S.-Z. ind.)	100-130
Ester value (E.-Z.)	65-125
Saponification value, cold (V.-Z. k.)	180-230
Soluble in 96 per cent. alcohol	78- 80 %
Ash	0·0-1·5 %

all from the natural drug, and not—as those obtained by Kremel, Beckurts and Brüche, and E. Dieterich—from extracts which do not correspond to the natural product.

The author, in this case also, examined the alterations produced in these normal values by adulterants, and arrived

at conclusions similar to those already stated in the case of Siam benzoin (*q.v.*).

Evans found 10·10–10·67 per cent. of matters insoluble in alcohol.

Gregor and Bamberger found the following methoxyl values (M.-Z.):—

Gregor	20·0–25·5
Bamberger	13·0–16·5

The detection of colophony by the Storch-Morawski reaction is described under “Colophony.”

19. Palembang Benzoin.

Origin and Habitat.—Not from *Styrax Benzoin*, but from other *Styracææ*, still unidentified, grown in farther India.

Chemical Constituents.—Impurities, 7·5 per cent.; no cinnamic acid, but benzoic acid and resin, 90–95 per cent. (Fr. Lidy).

General Properties, Commercial Varieties, Adulterants, etc.—See Siam benzoin.

Analysis :—

Beckurts and Brüche found—

	Sp. gr.	1·131
	Ash	2·38%
	Insolubility in alcohol	9·00%
From extract {	Acid value, d. (S.-Z. d.).	97
	Ester value (E.-Z.)	71
	Saponification value, hot (V.-Z. h.)	168

The last three values have therefore merely a relative worth.

The author has examined natural Palembang benzoin by the method he applied to the Siam and Sumatra varieties, and obtained the following values :—

Acid value, ind. (S.-Z. ind.)	113·40–130·90
Ester value (E.-Z.)	84·0 – 91·0
Saponification value, cold (V.-Z. k.)	198·0 –219·80
Ash	1·101–4·023%

20. Padang Benzoin.

Nothing is definitely known regarding the origin and chemical composition of this variety, except that, like Siam and Palembang benzoin, it is free from cinnamic acid (K. Dieterich).

For the general properties, commercial varieties, adulterants, etc., see Siam benzoin.

Analysis.—The author has examined the natural drug by his method, already described, and found—

Acid value, ind. (S.-Z. ind.)	121·80–124·60
Ester value (E.-Z.)	79·80– 81·20
Saponification value, cold (V.-Z. k.)	201·60–205·80
Ash	1·070%

21. Penang Benzoin.

Origin and Habitat.—Probably obtained from *Styrax subdenticulata*, Mic. (Styracæ). Farther India.

Chemical Constituents.—Benzoic acid, cinnamic acid, and resin ester (Fr. Lüdy).

For the general properties, commercial varieties, adulterants, etc., see Siam benzoin.

Analysis.—A. Kremel found the following values (from an extract):—

Acid value, d. (S.-Z. d.)	122·2
Ester value (E.-Z.)	57·9
Saponification value, hot (V.-Z. h.)	180·1

For reasons already mentioned, these figures possess nothing more than a merely relative value.

Evans found up to 6·17 per cent. of matters insoluble in alcohol.

The author subjected specimens of this variety to the method applied by him to other kinds of benzoin, and obtained the following results:—

Acid value, ind. (S.-Z. ind.)	121·80–137·20
Ester value (E.-Z.)	87·50– 91·70
Saponification value, cold (V.-Z. k.)	210·00–296·80
Ash	0·380– 0·773%

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22. Caranna Resin.

Resina Caranna.

Origin and Habitat.—*Icica* and *Amyris Caranna* and *Bursera acuminata* (Burseraceæ). Antilles.

Chemical Constituents.—Not yet closely examined, but at anyrate similar to elemi.

General Properties and Commercial Varieties.—Dense, lustrous, brownish green, resinous masses, mostly wrapped in leaves; it is easily softened, has a balsamic odour, and is to a large extent soluble in alcohol and ether. Employed to adulterate elemi (*q.v.*), with which it is often classified as an allied species. At present only rarely met with in commerce.

Protium Caranna (Burseraceæ), from Brazil, also yields a "Balsamo de Caranna," which, like other *Protium* elemis (Amessegá, etc.), is allied to true elemi.

Antilles Caranna resin is also considered by some as identical with Bourbon Tacamahac, from *Calophyllum Tacamahaca* (q.v., as also under elemi); and, in any case, it must be regarded as similar to elemi.

Adulterants.—Vegetable impurities.

Analysis.—The only reason for including this resin, which is now rarely met with (that in the market gives the impression of being an artificial product), is that it was and is used as an adulterant or surrogate of elemi.

Hirschsohn examined eleven kinds of Caranna resin, all of which, except two, he found to be completely soluble in alcohol, ether, or a mixture of both. The author has examined specimens of this resin, but cannot confirm Hirschsohn's opinion that it is identical with Bourbon Tacamahac (q.v.).

Examined by the usual method, Caranna resin from the Antilles gave the author the following values:—

	I.	II.
Acid value, d. (S.-Z. d) . . .	79·37	79·37
Ester value (E.-Z.) . . .	110·48	111·84
Saponification value, hot (V.-Z. h.)	189·85	191·21

According to these figures, Caranna does not seem to very closely resemble elemi, since the latter furnishes much lower values.

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23. Colophony.

Colophonium (officinal in German Pharmacopœia).

Origin and Habitat.—Various species of *Pinus*. Europe. Colophony is the anhydrous residue from the

distillation of the turpentine obtained from different trees of the *Pinus* family, especially *P. Laricio*, *P. Pinaster*, *P. Australis*, *P. Taeda*, and many others.

Chemical Constituents.—Chiefly abietic anhydride, with smaller quantities of acids allied to, isomeric, or polymeric with abietic acid. Also inert substances, pyrocatechuic acid, bitter principles, and slight traces of mineral constituents. No esters or their derivatives have been found, only resin acids, ethers, and lactones (the last-named according to Henriques).

General Properties and Commercial Varieties.—The colophonies form pale, nearly white to dark brown-red, and in any case almost transparent, masses; brittle, with a vitreous lustre, and furnishing a nearly white powder; they soften in the hand, and are completely soluble in hot alcohol. The different varieties are due to difference in the mode of heating—short and gentle, or prolonged and intense—employed in the preparation.

Whereas the paler kinds are considered more valuable, and more suitable for pharmaceutical purposes, other consumers prefer the dark-coloured sorts; the colour is therefore not a criterion of suitability, although a higher price is paid for the paler varieties.

Adulterants.—Owing to the low price of colophony, the only impurities that come in question are merely of a mechanical character, the more so because colophony itself forms a favourite adulterant for dammar, guaiacum, dragon's-blood, storax, benzoin, etc.

Analysis.—The detection of colophony and pine resin in pale resins can be effected by the Storch-Morawski reaction. The author, however, considers that it would be risky to form a definite opinion on the basis of this colour reaction alone, because various other resins, when dissolved in acetic acid,

also give a red coloration on the addition of sulphuric acid; and because this reaction is so general and far from specific that it cannot lay claim to any particular value, whilst for dark coloured resins it is altogether unsuitable.

Hitherto it has been the general practice to take the presence of esters in colophony for granted, and to determine the ester value, saponification value, and ether value,¹ as well as the sp. gr., solubility, ash, and acid value; but in the present state of knowledge with regard to the constituents of colophony, the ester and saponification value, and "unsaponifiable matter" determinations cannot be justified. The author, with a view to the introduction of uniformity in testing, has therefore proposed that only the sp. gr., ash, acid value, and degree of solubility should be determined.

Recently, Henriques—working on different lines to those previously followed by the author—has also succeeded in demonstrating the absence of esters. He has, however, found ethers and lactones, which apparently justify an "ether value" or "constant ether value," though not the so-called ester values hitherto ascribed to colophony.

The following values have been found by different authors:—

A. Kremel obtained—

	Pale.	Dark.	American.	English.
Acid value, d. (S.-Z. d.) .	163·2	151·1	173·0	169·1

by dissolving the samples in alcohol and titrating direct with alkali.

The circumstance observed by Williams that the acid value increased with the purity of the sample, was probably

¹ The author would propose the abbreviations, Ae.-Z. for "ether value, and K. Ae.-Z. for "constant ether value," in addition to the contractions already mentioned in the Introduction to Part II.

due to the kind of impurities present and the small percentage of undecomposed abietic anhydride. He found—

Water	0·13–0·34 per cent.
Ash	0·02–1·20 „

Von Schmidt and Erban found the following degrees of solubility :—

In Alcohol	} complete.
Ether	
Methyl alcohol	
Amyl alcohol	
Benzol	
Petroleum ether—almost complete.	
Acetone	} complete.
Glacial acetic acid	
Chloroform	
Carbon di-sulphide	
Oil of turpentine	
Acid value, d. (S.-Z. d.)	146·0
Saponification value, hot (V.-Z. h.)	167·1
Ether value (Ae.-Z.)	21·1

E. Dieterich found—

Acid value, d. (S.-Z. d.)	151·70–176·70
Sp. gr.	1·071–1·083

the former by direct titration in the same way as Kremel.

Beckurts and Brüche found—

	Red.	White.	Yellow.	Brown.
Sp. gr.	1·071–1·080	1·068	1·067	1·081
Acid value, d. (S.-Z. d.)	173–186	180	185	181
Ether value (Ae.-Z.)	0–12	0	0	0
Sapon. value, hot (V.-Z. h.)	179–193	180	185	181

also by direct titration. The term “ether” value has been used in this place instead of “ester” value, the researches of the author and Henriques showing it more suitable.

On the basis of his own experiments and numerous previously published values,¹ the author would propose—

¹ *H. A.*, 1896, 1897, *sub.* “Colophonium.”

(a) *Sp. gr. determination.*—A series of solutions of common salt, ranging between sp. gr. 1.070 and 1.085 at 15° C., are prepared, and in each of them are placed a few fragments of the colophony under examination, the aforesaid temperature being maintained. The sp. gr. of whichever solution retains the colophony in suspension will be that of the substance. In selecting the best pieces, care must be taken to reject such as exhibit cracks, air bubbles, or impurities.

The Mohr-Westphal balance can be advantageously used for colophony sp. gr. determinations, the usual method employed for beeswax¹ being pursued.

(b) *Acid value, ind. (S.-Z. ind.).*—One grm. of finely powdered colophony is suffused with 25 c.c. of alcoholic $\frac{n}{2}$ potash and left covered up for two hours — at anyrate until the whole is dissolved,—after which it is titrated back with $\frac{n}{2}$ sulphuric acid. The number of c.c. of combined KHO multiplied by 28.08 gives the acid value (indirect). No water should be added upon any account, and the potency of the alkali should be controlled by a blank experiment, without colophony.

The author finds that direct titration usually gives lower values than the indirect method, and aqueous alkali lower results than either method with alcoholic alkali. The above back titration gives values approximating most nearly to those furnished by theoretical calculation, and, in addition, the necessity for preparing a solution beforehand is obviated, the alkali serving both as a solvent and to combine with the acid. No water should be added, since this liquid decomposes the resin soap.

The author would set up the following standard of requirements in testing the purity of colophony in a uniform

¹ *H. A.*, 1897, p. 362.

manner, it being remarked that for technical and pharmaceutical purposes certain other criteria are required, which, however, must be left to the domain of these special branches, being too divergent to deal with in describing a uniform method. For example, a very pale colophony is preferable for pharmaceutical purposes, whereas in certain technical purposes colour plays no particular part.

“Colophony should be as light coloured as possible, and, when boiled with water and the extract tested with ferric chloride, should give only a minimum colour reaction. It should be almost entirely free from ash (or ponderable residue), and *completely* soluble in alcohol, ethereal oils, acetone, ether, chloroform, methyl alcohol, amyl alcohol, acetic ether, benzol, oil of turpentine, and carbon di-sulphide; and *partly* soluble in benzine, petroleum, and petroleum ether.

“The acid value (S.-Z. ind.) when determined by the above indirect method should vary between 145 and 185, and the sp. gr. between 1.045 and 1.085.”

The ether value, or Henrique's constant ether value (K. Ae.-Z.), can be determined by the “usual” hot saponification method (see Introduction to Pt. II.), and subtracting the acid value from the resulting saponification value.

Fahrion¹ has shown the untenability of the author's standard of 7 per cent. as the maximum percentage of matters insoluble in petroleum ether, it being found that a few good commercial sorts of colophony exhibit a larger amount of insoluble residue. The oxygen-absorption of colophony has been dealt with by Weger, in his treatise already cited.

Kitt found the carbonyl value (C.-Z.) = 0.54–0.56.

Gregor and Bamberger obtained negative results in the methoxyl value (M.-Z.) test.

¹ *Zeitschrift f. angewandte Chemie*, 1898, No. 34.

The following acetyl values (A.-Z.) were found by the author :—

Acetyl	{ Acid value (A.-S.-Z.) . . .	155·82–155·84
	{ Ester value (A.-E.-Z.) . . .	92·12– 95·37
	{ Saponification value (A.-V.-Z.)	251·21–274·94

the worth of which values was discussed in *Chem. Rev.*, 1898, No. 10 ; and the German Pharmacopœia tests for colophony were dealt with by the author in *Ph. C.*, 1898, No. 20.

As already mentioned, a discussion has been carried on by the author, Fahrion, Schick, and Heupel,¹ with regard to the determination of the acid, ester, ether, and saponification values. The author, on the basis of his researches, held colophony to be free from esters, and therefore incapable of having any ester value.

Henriques confirmed the absence of esters by other means, and recommended the direct estimation of the acid value and the determination of a “constant ether value” (K. Ae.-Z.), because he succeeded in showing the presence of ether and lactones in colophony. These discoveries terminated, in some respects, the debatable colophony question, since all that is necessary, in the absence of esters, is to rechristen the ester value (advocated by Schick, Fahrion, and Heupel) by the name “ether value,” in order to annul the previously existing chemical contradiction first exposed by the author. For this reason all the corresponding values have here been termed “ether values.”

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¹ *Zeits. f. angew. Chem.*, 1898, Nos. 12, 14, 17, 19 ; 1899, Nos. 2, 5, 8, 12.

A., 1889.—Mills and Muter, Ph. C., 1899, pp. 151 *et seq.*—Von Schmidt and Erban, Sitzgsber. Wiener Akad. d. Wiss., 1886, November part.—Storch-Morawski, Ph. C., 1889, p. 198.—Williams, Ph. C., 1889, p. 152.

24. Copal.

Resina Copal.

Origin and Habitat.—Certain species of *Trachylobium* and *Hymenæa* (Cæsalpinieæ) fossil, recent fossil, and recent resins. Africa, America, and East Indies.

Chemical Constituents.—Zanzibar copal is the sole variety that has been carefully examined. It contains trachyloic acid ($C_{54}H_{85}O_3 \text{ OH}(\text{COOH})_2$), 80 per cent.; isotrachyloic acid ($C_{54}H_{85}O_3 \text{ OH}(\text{COOH})_2$), 4 per cent.; α -copal resene ($C_{41}H_{86}O_4$), and β -copal resene ($C_{25}H_{38}O_4$), together 6 per cent.; impurities, 0.42 per cent.; ash, 0.12 per cent.; bitter principle and ethereal oil, 9.46 per cent. Trachyloic acid and its isomer are distinguishable by their different solubility, behaviour with lead acetate, and melting-point (C. Stephan).

Tschirch (*Ph. Ztg.*, 1899, No. 77) has recently isolated new "crystalline resinolic acids" by fractional extraction.

General Properties and Commercial Varieties.—The name copal is a generic term. In England, anime is synonymous with copal (see Anime).

Copals vary in appearance according as they are in the crude, decorticated, or washed condition. They are nearly all more or less vitreous, transparent, yellow to red in colour, and with or without a faceted surface (goose skin), the latter being specially characteristic of Zanzibar copal. The following principal fossil, semi-fossil, and recent varieties have been identified:¹—East African, West African, South American, East Indian, and Kaurie copal.

¹ See the treatises of Gilg, *Chem. Rev.*, 1898, Nos. 8, 9; Zucker, *Ph. Ztg.*, 1898, p. 848; *Dingler's Polytech. Journ.*, 1897, p. 212; Bocquillon, *Rép. de Pharm.*, series 3 vol. ix., 1897, No. 8; Wiesner's *Techn. verw. Bals.-Harze, Gummiharze*, 1869, pp. 144–168.

These larger classes may be subdivided into—

East African.—Zanzibar (best and hardest kind, m.p. over 400°C.), Mozambique, Madagascar.

West African.—Young copal, from Sierra Leone; flint copal; Gaboon, Loango, Angola, Benguela, and Congo copal.

Benguela and Angola copal are known in commerce as “Ocota Cocota” and “Muccocota” gum.

American.—Courbaril copal (from *Hymenæa Courbaril*) and copal from other species of *Hymenæa*, such as *Hymenæa admirabilis*, *stilbocarpa*, etc., also known as “Anime” (*q.v.*).

East Indian.—Manila copal, from *Vateria Indica* (*Dipterocarpeæ*), also known as “white dammar” (*q.v.*).

Kauri Copal, from *Damara Australis* (*Coniferæ*), also known as “New Zealand dammar.”

White Zanzibar copal, or Zanzibar copal in balls, is sold in Zanzibar as “tree copal”; it is of low quality, soft, and recent. “Chakazzi” copal mostly comes into commerce as “Zanzibar copal without goose skin.”

As copal is frequently shipped to a distance for washing, Zanzibar copal has also been met with under the names “Salem” and “Bombay” copal, there being large copal-washing works in the United States, whilst a good deal of copal used to come on the market *viâ* Bombay.

For rare types of copal, such as Inhambane and Accra copal, see Gilg’s treatise already cited. According to the latest researches of this worker, both Madagascar and Zanzibar copal are derived from the same tree, *Trachylobium verrucosum* (which is identical with *T. mossambicum*). They certainly exhibit many characteristics in common.

According to Wiesner, copals can be marked (scratched) by calspar; some varieties—Sierra Leone, Gaboon, Angola—are of equal hardness with rock salt. Zanzibar and Mozambique copal are between rock salt and copper sulphate in

point of hardness; whilst Benguela, Kauri, and Manila copal are less hard than rock salt. The scale of hardness may therefore be arranged as follows:—(1) Zanzibar copal, (2) Mozambique, (3) Sierra Leone (flint copal), (4) Gaboon, (5) Angola, (6) Benguela, (7) Kauri, (8) Manila, and (9) Courbaril copal.

The East African copals are fossil, those from West Africa semi-fossil, the Kauri copals semi-fossil, the South American kinds recent; but nothing definite in this respect is known of the Indian copals.

According to Worlée, the “hard” copals are:—Zanzibar, Sierra Leone, Benguela, and Angola copal; the “soft” copals being—West Indian, ball Kauri, and Manila copal; whilst Zucker adds Accra copal to this latter class.

The copals are distinguished in commerce according to colour—white, pale, or dark red; condition—natural, half-shelled, or shelled; and other peculiarities. For the distinction between true copals and amber, or the resins from *Coniferæ* and *Dipterocarpeæ*, see under “Analysis.”

Adulterants.—False, soft copals, coniferous and dipterocarpous resins and amber.

Analysis.—Of the unusually large number of copals, all of which are valued according to the degree of hardness and the corresponding insolubility in alcohol, but few analytical details are available. The solubility and fusibility vary with the origin and age, the melting-points ranging from 180°–340° C., the hardest kinds being the most refractory. In alcohol the soft varieties are only partially soluble, the harder kinds scarcely at all. Rosemary oil and Cajeput oil dissolve nearly all copals, but not amber; and nearly all are soluble in oil of turpentine, especially after being melted or distilled—even such as were previously untouched by this solvent—so that almost all are rendered completely soluble

therein, or in fatty oils, etc., a property which is of high technical importance. Many copals, too, when they have been exposed for a long time in sunlight, and have absorbed oxygen, become soluble, or at least more soluble than before. According to Andres, the copals are soluble in strong (anhydrous) alcohol, provided they have previously been left to swell up in ether; and mixtures of absolute alcohol and oil of turpentine are said to form a good solvent for soft copals. Andres recommends a mixture of carbon di-sulphide, oil of turpentine, and benzol (equal parts) as the best solvent for unmelted, undistilled copal. To convert the copals into a soluble form, the usual practice is to heat them to 200° – 220° C. for several days, or else distil them, dry (until twenty-five per cent. of copal oil, which is afterwards used as a solvent, has passed over)—the temperature employed being 380° – 400° C. The copal is then soluble in oil of turpentine, the degree of solubility varying with the amount of copal oil distilled over.

The following table compiled by Violette shows the results furnished by 100 grms. of copal:—

Loss of Weight on Distillation.	Amount of Oil Collected.	Behaviour of the Distilled Copal in Presence of Oil of Turpentine.
Grms.	Grms.	
3.0	3.0	Insoluble.
9.0	8.5	Do.
10.5	10.2	Do.
16.0	15.7	Do.
20.0	19.0	Somewhat soluble.
22.0	21.3	More readily soluble.
25.0	24.5	Very readily soluble.
28.0	27.1	Do. do.
30.0	29.0	Do. do.
32.0	31.0	Do. do.

In practice only about 10–12 per cent. is generally distilled off.

Both copal oil and amber oil are employed for dissolving soft grades of copal.

What the copals and ambers gain in solubility by distillation they lose in point of colour (paleness). It may also be mentioned that the copals are used for the preparation of lacquer varnishes (solutions of melted copal in linseed oil varnish) and ordinary lacquers (resin solutions without varnish).

The sp. gr. is given by Meichel and Stingel as 1·062–1·149, and by Brisson as 1·045–1·390. Tables have been drawn up for the differentiation of hard and soft copals, but though the data—like those given by older authors (Dierbach, Perrolet, Hanbury, Daniell, Gisecke, Lindemann, Wachsmuth, Jonas, Constantini, Böttger, Heeren, and others)—contribute to some extent to the characterisation of the copals, they are not as a rule directly useful, being in many cases contradictory.

Williams determined the moisture in a number of specimens as 0·57–2·41 per cent., and the ash 0·27–2·06 per cent., with the following other values by the usual method:—

Copal.	Acid Value, direct (S.-Z. d.).	Ester Value (E.-Z.).	Sapon. Value, hot (V.-Z. h.).
Manila	136·0	52·5	188·5
Borneo	144·0	35·3	179·3
Singapore	128·8	65·3	194·1
Sierra Leone	84·0	45·0	129·0
Red Sierra Leone	72·8	65·7	138·5
Red Accra	46·2	85·4	131·6
White Angola	57·4	75·6	133·0
Red Angola	60·2	76·0	136·2

As the true copals, such as Zanzibar copal, have been found to contain no esters, the above ester and saponification

values must be accepted with some reserve, the more so because the dipterocarpous resins (such as Manila copal from *Vateria Indica*) may also be free from esters, like the dammars.

According to Hirschsohn, petroleum ether will take up only 6·5 per cent. of good African copal. Alcohol dissolves only 25 per cent. of the best copals; and the solubility in chloroform varies inversely with the hardness, 42 per cent. of best East Indian copal, 52 per cent. of African, and 46 per cent. of Angola copal being dissolved, whilst Kauri and Brazilian sorts are completely soluble.

[TABLE.

Von SCHMIDT and ERBAN give the following Solubilities:—

Copal.	Alcohol.	Ether.	Methyl alcohol.	Amyl alcohol.	Benzol.	Petroleum ether.	Acetone.	Glacial acetic acid.	Chloroform.	Carbon di-sulphide.	Oil of turpentine.
I. Natural.											
Zanzibar	insol.	partly sol.	insol.	sparingly sol.	partly sol.	insol.	insol.	partly sol.	partly sol.	insol.	partly sol.
Red Angola	insol.	partly sol.	partly sol.	sol.	partly sol.	partly sol.	partly sol.	partly sol.	partly sol.	almost sol.	partly sol.
White do.	insol.	partly sol.	insol.	partly sol.	partly sol.	insol.	insol.	partly sol.	partly sol.	almost sol.	almost insol.
II. Shelled.											
Zanzibar	almost sol.	partly sol.	insol.	partly sol.	almost completely sol.	insol.	almost sol.	partly sol.	partly sol.	nearly sol.	almost completely sol.
Red Angola	partly sol.	almost completely sol.	sparingly sol.	sol.	partly sol.	almost insol.	sparingly sol.	partly sol.	sol.	nearly sol.	almost completely sol.
White do.	partly sol.	partly sol.	sparingly sol.	partly sol.	partly sol.	almost insol.	almost insol.	partly sol.	partly sol.	nearly sol.	almost completely sol.

Von Schmidt and Erban give the following values for copals :—

Copal.	Acid Value, direct (S.-Z. d.).	Ester Value (E.-Z.).	Sapon. Value, hot (V.-Z. h.).
Melted white Angola .	95·5	24·8	120·3
Melted red Angola .	30·2	80·0	110·2
Unmelted red Angola .	—	—	147·3
Unmelted white Angola .	—	—	131·0
Unmelted Zanzibar .	—	—	91·0
Melted Zanzibar .	—	—	35·7

which, however, do not well agree with those found by Williams.

Special mention should be made of Friedburg's studies on copal resins. He states that hard copal is insoluble in alcohol, ether, and oil of turpentine, though it dissolves in the two latter after having been heated. When heated no higher than 182° C. the copal escapes decomposition, and forms, on cooling, a highly lustrous, vitreous, translucent resin, readily soluble in cold or warm oil of turpentine. Copal is soluble in aniline and its homologues, as also in nitrobenzol and chloroform; phenol and cymol likewise form good solvents for copal. Benzaldehyde dissolves copal completely at first, but soon the mass thickens (owing to the condensation of resin acids, etc., with aldehydes?). Glacial acetic acid partly dissolves copal; and carbon di-sulphide is taken up in large amount, forming a colloid which becomes brittle on drying. According to Friedburg there are three classes of copals—soft, semi-hard, and hard. With regard to the solubility of copal in chloral hydrate (see below) mention is deserved by Fleming's patented discovery of the solubility of copal in epi- and di-chlorhydrin. Valenta recommends such solutions of copal or other resins as a pellicle for supporting the emulsion on photographic negatives.

For distinguishing true copals from coniferous and dip-terocarpous resins, Mauch recommends the chloral hydrate test—true copal being insoluble in an 80 per cent. solution of this reagent, whilst dammar, colophony, Kauri and Manila copal are either partially or completely soluble therein. Zucker proposes the following test for distinguishing hard copals from the soft varieties:—The sample is suffused with boiling water, and left to stand for half an hour. Hard copal remains unaltered, but the soft kinds become milky and opaque.

With reference to the foregoing analytical data, it may be mentioned that the saponification values have also been determined, as well as the acid values, but are of merely relative worth, since we now know that the copals, both the true kinds and those resembling dammar, consist of only neutral bodies and resin acids, and are free from esters. These conditions have already been referred to by Kremel, who also gives for copal (which he calls dammar) from *Vateria Indica* the acid value (S.-Z. d.) 15·4, while for the other copals he gives 127–147. The author recently examined Zanzibar copal, and found that direct titration gives unduly low results; that an addition of water decomposes the resin soap; that existing values are unreliable; and that back titration is the best method of determining the acid value in copal. Already, in the case of dammar, sandarach, etc., he found that titration in an alcoholic liquid gave unreliable and irregular acid values, owing to the fact that the resinolic acids are not so easily or rapidly neutralised by the alkali, and, consequently, they are best treated by his back titration method. With Zanzibar copal similar conditions obtain, the titration going on too slowly to yield reliable values when the copal is dissolved in ether-alcohol, as practised by Kremel. By the direct method, he found

the acid value 15–20, whilst Kremel, working in the same manner, gives 130–150, which must either be a printer's error for 13–15, or an error due to some defect in the titration; and, in fact, the author's experiments on this point indicate the use of water as the source of the discrepancy. Kremel added water to dissolve the salts during titration, an erroneous procedure, since it causes the decomposition of the resin soap. If the titration be completed without water, and then some of that liquid added, the red coloration at once vanishes, a sign that the water has decomposed the resin soap and that secondary reactions have occurred.

In the same manner, an addition of water at the end of the back titration process will eliminate the red coloration, thus indicating the liberation of alkali. The difference in the consumption of alkali when working with and without water may amount to as much as 2 c.c., which probably explains the excessively high values given by Kremel; in fact, the deficit, due to insufficient combination with the resin acids, in the direct titration method employed by Kremel was converted into an excess by the secondary reactions ensuing on the addition of water.

The author proceeds on the following lines:—

Acid value, indirect (S.-Z. ind.).—One grm. of finely pulverised Zanzibar copal is placed in a glass-stoppered flask and suffused with 25 c.c. of benzine, 25 c.c. of ether, and 20 c.c. of alcoholic $\frac{n}{2}$ potash. The closed flask is left at room temperature for twenty-four hours, and the contents are then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water.

The resulting acid value is, in the case of Zanzibar copal, between 60 and 65.

Intermediate members between the copals and the dammars and Kauri copal, as well as adulterations with

amber, may be detected by the aforesaid relative solubilities and behaviour with chloral hydrate, as also by their behaviour towards Cajeput oil, and their abnormal acid values (S.-Z. ind.). Moreover, amber gives ester and saponification values, copal only the indirect acid value (see also Amber, and Kremel's paper on Copal and Amber, in *N. z. P. d. A.*, 1889).

The acetyl, carbonyl, and methoxyl values of Zanzibar copal have also been determined of late, the author finding—

Zanzibar Copal.	Acetyl.		
	Acid Value (A.-S.-Z.).	Ester Value (A.-E.-Z.).	Saponification Value (A.-V.-Z.).
Soluble portion	77·71	125·58	203·29
Insoluble portion	210·10-221·14	84·80-111·17	305·94-331·27

Kitt found, for East Indian copal, the carbonyl value (C.-Z.) 0·61; and Gregor and Bamberger both obtained negative results with the methoxyl test (M.-Z.). (For the worth of these values, see *Chem. Rev.*, 1898, p. 10.)

The so-called "ester resins" serving as competitors of, and substitutes for, copal have been described by Zucker (*Ph. Ztg.*, 1898, p. 848).

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25. Dammar.

Resina Dammar (official in German Pharmacopœia III.).

Origin and Habitat.—Certain species of *Dammara* and *Hopea* (Burseraceæ and Dipterocarpeæ). Southern India.

Chemical Constituents.—Dammarolic acid ($C_{54}H_{77}O_3$ ($COOH$)₂), 23 per cent.; α -dammar resene ($C_{11}H_{17}O$), 40 per cent. soluble in alcohol; β -dammar resene ($C_{31}H_{52}O$), 22·5 per cent. insoluble in alcohol, soluble in chloroform; ethereal oil and bitter principle, 0·5 per cent.; moisture, 2·5 per cent.; ash, 3·5 per cent.; impurities, 8 per cent. (Glimmann).

With regard to the "crystalline resinolic acids" recently isolated by Tschirch by fractional extraction, see *Ph. Ztg.*, 1899, No. 77.

General Properties and Commercial Varieties.—East Indian Sumatra dammar is in the form of stalactitic granules and lumps, yellowish, transparent, coated with dust, of vitreous conchoid fracture, and harder than colophony. When chewed, dammar breaks down to a white powder, and it melts at 180° C. It is completely soluble in petroleum ether or chloroform, but only partially so in alcohol or ether. The intermediate resins between dammar and copal, such as Australian (or New Zealand) dammar = Kauri copal, are readily distinguishable (see below).

Among the dammars are grouped also—Saul resin, from *Shorea robusta* (Dipterocarpeæ, Sumatra and Java); Dammar Rata Kûtsching (Singapore), from *Hopea micrantha splendida*; and Dagiang, or Rose, dammar (Borneo and Malacca), from *Retinodendron Rassak*; Selo-dammar (Singapore), from *Artocarpus integrifolia*; and "black dammar," of unknown origin (*Canarium strictum*, East Indies, and *C. rostratum*, Molucca Islands [?]). All these are rarely met with in European markets. Manila copal (*q.v.*), from *Vateria Indica*, is also called "white dammar."

The origin of the dammars has been dealt with by C. Müller in a valuable paper (*Ber. d. Deutsch. pharm. Ges.*, 1891, p. 365).

Adulterants.—Colophony, Australian dammar (Kauri copal).

Analysis.—As is well known, the generic term “dammar” includes a number of resins from trees of the families *Dipterocarpeæ*, *Burseraceæ*, and *Coniferæ*, as well as transitions into the copal group (such as Australian dammar, or Kauri).

For distinguishing copals from dammars, and the latter again from conifer resins—which also, to some extent, figure as “dammar” in commerce,—the Mauch chloral hydrate test may be recommended. True copals (*q.v.*) do not dissolve at all in 80 per cent. chloral hydrate solution, whereas true dammars, from *Dipterocarpeæ*, on the other hand, cede certain quantities to this solvent, the reaction being accompanied by a characteristic increase in volume; and conifer resins—like Kauri copal = West Indian dammar—are completely soluble. The solubility of the resins in epì- and di-chlorhydrin (Valenta) has already been referred to in Part I.; and mention may here be made of Hirschsohn’s researches on twenty-three varieties, with the following results:—

Dammar	Solubility in—	
	Petroleum Ether.	85 per cent. Alcohol.
	per cent.	per cent.
East Indian . .	88·03	87·97
American . .	83·42	83·90
Dammar in massis .	77·18	77·60
East Indian . .	84·09	84·89
D. <i>viridis</i> . .	73·13	57·65
Do. . .	75·46	57·77
D. <i>nigra</i> . .	83·81	—
D. <i>marmorata</i> . .	54·12	53·98
Do. . .	30·20	29·99

The soluble constituents were dried at 120° C.

In utilising dammar for varnish-making, the resin is melted, like copal and amber, by which means it becomes soluble. A mixture of alcohol and oil of turpentine forms a good solvent. Weger (*l.c.*) has dealt with the absorption of oxygen by dammar when exposed to the air in thin layers.

Attention was bestowed on the examination of dammar by Brandes, Thomson, Dalk, Labillardiere, Giesecke, Müller, Mäusel, and others; and subsequent communications were made by Mills and Muter, von Schmidt, Erban, Kremel, Schweissinger, Williams, E. Dieterich, K. Dieterich, Gregor, Bamberger, and Mauch. (For the detection of colophony in dammar, by the Storch-Morawski reaction, see Colophony.)

Williams found—

Ash	0·01– 0·07 per cent.
Moisture	0·33– 0·85 „
Acid value, d. (S.-Z. d.). . .	21·00–26·00

the last-named by the usual method. As dammar contains no ester, the saponification value found by this worker has only relative worth.

Von Schmidt and Erban found the following degrees of solubility in—

Alcohol	partial.
Ether	„
Methyl alcohol	„
Benzol	complete.
Petroleum ether	almost complete.
Acetone	partial.
Glacial acetic acid	„
Chloroform	complete.
Carbon di-sulphide	„
Oil of turpentine	„

Acid value, direct (S.-Z. d.), by usual method = 31·8.

E. Dieterich found 0·85 per cent. of moisture.

A. Kremel rightly confined himself to the direct acid value, in working with the usual method, and found—

	Acid value, d. (S.-Z. d.).
Dammar	31·0
Do.	34·3
Do. (orient.)	34·2

For “white dammar,” which is identical with Manila copal (*q.v.*) from *Vateria Indica*, the same worker obtained the acid value, d. = 15·4.

According to Glimmann, dammar is completely soluble in benzol, chloroform, and carbon di-sulphide; and partially so in alcohol, toluol, acetone, aniline, petroleum ether, and acetic acid.

The researches of Graf, Tschirch, and Glimmann having shown that dammar is free from esters, the hot saponification and ester values determined by nearly all the above-named workers—except K. Dieterich—have to be discarded. E. Dieterich very rightly concluded that, in view of the great fluctuations recorded in the ester value, it had better be left out of consideration.

The author has also shown that direct titration often gives unduly low acid values for dammar, because the resin acid—especially in presence of the neutral constituents, and owing to the low acidity of dammarolic acid—does not always combine quantitatively. Hence, in the author's view, the values from direct titration are inferior to those furnished by the indirect method. He works on the following lines by indirect titration, which offers the additional advantage of dispensing with a preliminary process of solution:—

(a) *Acid value, ind.* (S.-Z. ind.).—One grm. of dammar is suffused with 50 c.c. of benzine (sp. gr.

0.700), followed by 20 c.c. of alcoholic $\frac{n}{2}$ potash, the whole being then left for twenty-four hours, and afterwards titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water. The acid value (indirect) is the product of the consumed volume (c.c.) of KHO multiplied by 28.08.

(b) *Ash determination.*—Two grms. of the drug are carefully incinerated and calcined until constant, the weighings being made after cooling down in a desiccator.

Formerly, the author employed alcoholic and aqueous alkali for the acid-value test, but found that the alcoholic solution alone is quite sufficient; and indeed, in the case of samples of dammar adulterated with colophony, it is particularly advisable to dispense with aqueous alkali, since the presence of water would lead to the decomposition of the colophony resin soap and furnish unreliable values. Consequently it is best to work with alcoholic alkali alone. The extreme limits of acid value obtained by the author with this method are 20–30; and the maximum permissible ash content is 0.1 per cent.

Dammar is often adulterated with colophony, for the detection of which Schweissinger recommended Kremel's acid value (direct) test. More recently the author has detected such adulteration by the abnormally high acid values (indirect) obtained by his own method, described above; and has also shown that commercial dammar powder is impure and gives abnormally high acid values. Thus, dammar with 25 per cent. of colophony gave the acid value (indirect) 56.33–58.00, and with 50 per cent. 96.49–97.68, these results confirming the suitability of the method for this purpose. The Hirschsohn test, which furnished good results in the hands of E. Dieterich, can also be recommended as a qualitative method for detecting

colophony in dammar. The sample is suffused with ammonia, and the liquid after filtration is supersaturated with acetic acid, whereupon, in the absence of colophony, the filtrate remains clear; but when colophony is present a precipitate is formed, the colophony being soluble in ammonia but thrown down in presence of acid. If the proportion of colophony be large, the entire acid liquid will become gelatinous.

For black dammar (probably from *Canarium rostratum*) and dammar from *C. strictum*, the following values have been obtained:—

	Acid Value, ind. (S.-Z. ind.).
Black dammar	49·14–53·53
Dammar from <i>C. strictum</i>	73·01–74·41

The author has recently found the acetyl values for dammar to be as follows:—

Acetyl acid value (A.-S.-Z.)	50·52– 51·80
Do. ester value (A.-E.-Z.)	81·56– 83·06
Do. saponification value (A.-V.-Z.)	132·08–134·86

Gregor and Bamberger obtained only negative results with the methoxyl value (M.-Z.) test.

(For the worth of these values, and of the German Pharmacopœia tests, see references already cited under Colophony.)

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26. Dragon's-Blood.

Resina Draconis.

Origin and Habitat.—I. Palm dragon's-blood, from *Dæmonorops Draco*, Bl. (Palmæ); II. Socotra dragon's-blood, from *Dracæna Cinnabari* (Dracænæ). South-eastern Asia, Socotra, West Indies, America.

Chemical Constituents.—I. Palm dragon's-blood. Dracoalban ($C_{20}H_{40}O_4$), 2·5 per cent.; Dracoresene ($C_{20}H_{44}O_2$), 13·58 per cent.; benzoic dracoresinotannol ester ($C_6H_5COOC_8H_9O$); and benzoylactic dracoresinotannol ester ($C_6H_5COCH_2COOC_8H_9O$)—forming together a pure red resin,⁹ or phenyl- β -monoxyacrylic dracoresinotannol ester (?)—56·86 per cent.; resin insoluble in ether, 0·33 per cent.; phlobaphene, 0·03 per cent.; vegetable residue, 18·40 per cent.; ash, 8·3 per cent. (K. Dieterich.)

II. Socotra dragon's-blood.—Pure resin ($C_{18}H_{18}O_4$)—the author has recently found this to be a mixture of several resins, and not a definite chemical entity,—83·35 per cent.; gum, 0·7 per cent.; matter soluble in carbon di-sulphide, 0·48 per cent.; vegetable residue, 12 per cent.; mineral matter, 3·5 per cent. (Lojander.)

The following varieties contain benzoic acid, but no cinnamic acid:—Socotra, so-called “vera”; dragon's-blood, from *Dracæna Ombet Kotschy*; Socotra dragon's-blood, “sicut dicta,” from *Dracæna Chizantha*, B.; and Palm dragon's-blood, from Banejrmasin (Borneo). The last-named contains dracoalban, whereas the others are deficient in this substance. (K. Dieterich.)

General Properties and Commercial Varieties.—Palm dragon's-blood (Sumatra) in bast is in the form of sticks, about eight inches long, and one-half to one inch thick, wrapped in *Ligula* leaves. Outside, it appears brown, but

shows a red, lustrous fracture, and gives a light, red powder. On paper it leaves a red mark, and it is almost entirely soluble in alcohol and ether. The grade "in massa" is poor, and generally adulterated. Palm dragon's-blood alone answers to the author's "draco-alban" test, and is thus distinguishable from the *Dracænæ* varieties.

Socotra dragon's-blood occurs as irregular lumps of conchoid appearance, somewhat pitted, and of dark brownish red, lustrous colour. The fracture is pale, lustrous red, and the powder also light red. The substance is only partially soluble in alcohol and ether, and contains no draco-alban.

American (Mexican) and West Indian dragon's-blood, from *Pterocarpus* (*Croton*) *Draco*; dragon's - blood, from Venezuela and Columbia, and a few similar resins, are more nearly allied to Kino (*q.v.*) than to dragon's-blood, or are entirely obsolete. At present, Sumatra palm dragon's-blood is the only kind in commerce.

Adulterants.—Ferric oxide, bole, artificial products made of resin, sandal-wood, gum, and colophony.

Analysis.—The commercial varieties of dragon's-blood are fewer than formerly, Sumatra palm dragon's-blood "in bast" and "in mass" being the principal kind. The technical application of this resin—for varnish in particular—is also very restricted. Analytical data are still very scanty, though adulterations with conifer resins and ferric oxide have been reported by several workers;—Bretet citing an artificial product made of resin and powdered sandal-wood. Hirschsohn states that adulterated specimens are more soluble in petroleum ether than the pure drug.

Hilger and Wittstein report on adulterated products which can be distinguished at the first glance. Von Schmidt and Erban, and E. Dieterich, made iodine value determinations, which, however, were so irregular in their

results as not to be worth mention. (For the detection of colophony by the Storch-Morawski reaction, see Colophony.)

Von Schmidt and Erban also found that dragon's-blood is only partially soluble in alcohol, ether, methyl alcohol, amyl alcohol, benzol, petroleum ether, acetone, glacial acetic acid, chloroform, carbon di-sulphide, and oil of turpentine; and the following degrees of solubility were determined by the author, for Sumatra dragon's-blood:—

Alcohol	}	readily soluble.
Ether		
Benzol	}	partially soluble.
Chloroform		
Acetic ether		
Petroleum ether		
Carbon di-sulphide		

Von Schmidt and Erban characterised the solubility in ether and alcohol as partial, merely because the vegetable residue necessarily remained undissolved.

(On the solubility of dragon's-blood in epi- and di-chlorhydrin (Valenta), see table in Part I.)

The table drawn up by Hirschsohn for differentiating the various kinds of dragon's-blood is now no longer applicable. Williams found 9·34 per cent. of water, and 3·58 per cent. of ash, and also determined the acid and ester values. As, however, dragon's-blood contains no free acids, the acid values obtained are of merely relative worth. The same worker obtained the (hot) saponification value (V.-Z. h.), 153·4, by the usual method.

Gregor and Bamberger determined the methoxyl value (M.-Z.) to be—

I.	II.	III.
27·6	25·3	33·8

Kitt obtained the carbonyl value (C.-Z.), 0·92.

The following acetyl acid values (A.-S.-Z.) were found by the author :—Palm dragon's-blood, 139·07–139·79 ; but the corresponding ester and saponification values could not be determined, owing to the dark colour of the solution. (For the worth of these determinations, see *Chem. Rev.*, 1898, No. 10.)

The author examined a number of varieties of dragon's-blood by his own fractional saponification method. The following procedure being adopted for determining the resin value (H.-Z.) and gum saponification value (G.-V.-Z.) :—

(a) *Resin value* (H.-Z.).—One grm. of dragon's-blood is suffused with 50 c.c. of ether and 25 c.c. of alcoholic $\frac{n}{2}$ potash, and left in a closed, glass-stoppered flask for twenty-four hours, the contents being then mixed with 250 c.c. of water and 100 c.c. of alcohol, and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The resin value is the product of the volume (c.c.) of KHO consumed, multiplied by 28·08.

(b) *Gum saponification value* (G.-V.-Z.).—One grm. of dragon's-blood is suffused with 50 c.c. of ether and 25 c.c., of alcoholic $\frac{n}{2}$ potash, and left for twenty-four hours in a closed flask, at the end of which time it receives an addition of 25 c.c. of aqueous $\frac{n}{2}$ potash, and, after standing twenty-four hours longer, is titrated back with $\frac{n}{2}$ sulphuric acid, in presence of phenolphthalein as indicator,—250 c.c. of water and 100 c.c. of alcohol having been previously added. The volume (c.c.) of KHO consumed, multiplied by 28·08, gives the gum saponification value.

(c) *Draco-alban test*.—Ten grms. of powdered dragon's-blood are extracted with 50 c.c. of hot ether, the resulting solution being then concentrated to about 30 c.c. and poured into 50 c.c. of absolute alcohol. After leaving to settle for an hour, a white flocculent precipitate will be observed. (Characteristic for palm dragon's-blood alone !)

The extreme limits of the above values determined by the author are as follows :—

A. Resin value (H.-Z.)	79·80-119·00	} Palm dragon's-blood.
Gum saponification value (G.-V.-Z.)	86·80-173·20	
Draco-alban test—positive.		
B. Resin value (H.-Z.)	81·20- 87·40	} Socotra dragon's-blood.
Gum saponification value (G.-V.-Z.)	92·40- 95·40	
Draco-alban test—negative.		

He finds the draco-alban test to be characteristic of Palm dragon's-blood alone, and not for the varieties obtained from *Dracaena*.

An addition of colophony—which seems to be a regular thing in the grades sold “in mass”—can be detected by the abnormally high resin value and gum saponification value; and in such event Palm dragon's-blood answers very slowly to the draco-alban test.

According to Mauch, both Palm dragon's-blood and that from *Liliaceæ* are soluble in 80 per cent. chloral hydrate solution.

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27. Elemi.

Resena Elema.

Origin.—Various Burseraceæ, such as *Icica Icicariba*, *Amyris Plumieri*, and certain species of *Canarium*, like *C. commune*. According to Tschirch, Manila elemi is certainly derived from *C. commune*. The name elemi is generically applied to a large number of resins.

Habitat.—The Philippines, Central and South America, East and West Indies, Africa.

Chemical Constituents.—Manila elemi, or, as it is mostly termed in commerce, “soft elemi,” is the only kind that has been closely examined. It contains—crystalline resin = amyrin ($C_{15}H_{42}O$), 25 per cent.; ethereal oil (dextrophellandrene, $C_{10}H_{16}$, and dipentene, $C_{10}H_{14}$), 10 per cent.; amorphous resin, 60–70 per cent.; small quantities of elemic acid ($C_{35}H_{46}O_4$), bryoidin ($C_{20}H_{38}O_3$), and bitter principle (Flückiger). Amyrin, again, consists of two substances, with the formula $C_{30}H_{48}OH$ — α - and β -amyrin,—which are isomeric, and can be separated as acetyl derivatives (Vesterberg).

General Properties and Commercial Varieties.—When fresh, elemi is a clear and light-coloured solution of resins in ethereal oil, with a portion of the resin crystallised out. Manila, or “soft,” elemi is sometimes a viscid mass, rendered turbid by a crystalline deposit; at others, a soft, semi-crystalline, yellow resin, which may be quite hard, and is then sold as “hard” elemi, its value being inferior to that of the soft variety. The smell of the fresh substance recalls lemons, fennel, mace, or good oil of turpentine.

American, or West Indian, Yucatan elemi generally forms “hard” commercial elemi. Formerly “soft” Yucatan elemi was to be had, but this is rarely the case now.¹ Mexican, or Vera Cruz, elemi comes from *Amyris elemifera*, and is closely allied to Caranna resin (*q.v.*), from *Amyris Caranna*. Gum copal (or gum opal), from *Dacryodis hexandra* (a tree known in St. Lucia as “gomier à canots,” on account of its resin being used for boats), is also a kind

¹ As a rule, “soft elemi” is now understood to mean Manila elemi, and “hard elemi” that from Yucatan. This, though incorrect, is explainable by the fact that commercial Manila elemi is now generally soft, whilst Yucatan is nearly always hard.

of elemi; and Cayenne incense, from *Icica heptaphylla*, is placed in the same class.

Brazilian Rio-elemi is a mixture of resins from species of *Protium*; and, according to Peckolt, one of the protium elemis is known in Brazil as "Almessega," and is probably derived from *Protium heptaphyllum*, M., var. *Brasilense*, Engl.

In addition to the last-named resiniferous tree, *P. h.*, var. *venenosum* and *P. Brasilense*, Engl., are also found in Brazil. Certain varieties similar to elemi are also known by the names—Resina tacamahaca, kikekunemalo, Resina caranna, Resina anime, the reason of this being that "elemi" is a generic term. East Indian elemi is said to come from *Canarium zephyrinum* (Moluccas).

African elemi (packed in bast like dragon's-blood) is derived from *Boswellia Freriana*, and is known as "Luban Matti"; it comes from Somaliland, *viâ* Cape Gardafui, and was formerly considered as a kind of incense (*q.v.*). Gomart gum from *Bursera gummiifera* is a species of elemi, and has been recommended as a substitute for mastic (*q.v.*); this same gum is also classed along with incense (*q.v.*), the parent tree—also called "gommier"—being ranked with the so-called West Indian "incense trees." It should, however, be more properly relegated to the elemi group, in the same way as Occumé resin from West African (Gaboön) *Burseraceæ*. Numerous species of *Icica* furnish other varieties of elemi, now no longer met with in commerce. Resina Hedwigiae¹ (*Hedwigiae balsamifera*, *Burseraceæ*) and Resina Hyowæ are also counted as elemis, the second in particular being nearly allied to Caranna resin (see Flückiger's *Pharmacognosie*, p. 88). Other intermediate members between elemi and the incense

¹ The balsam from *H. balsamifera*, the "baume à cochon" (hog balm), acts like copaiba (*q.v.*); its resin is the said Res. Hedwigiae, and is classed by Hirschsohn as allied to elemi. (See Table on next page).

group are not by any means rare (see under Incense, Caranna, Tacamahac, and Anime).

Apart from Manila and Yucatan elemi, all the known varieties are met with in the "hard" form exclusively.

The author has drawn up the following table of elemis, which, however, does not exhaust the list, though containing all the most important resins. (Tschirch groups the elemis with the resene resins—see Classification of Resins.)

I. True Elemis—

Soft and hard.	{	Manila elemi; from <i>Canarium commune</i> ; generally met with in commerce in the "soft" state, but also sometimes as "hard."
		American or West Indian, Yucatan elemi; probably from <i>Amyris Plumieri</i> ; usually "hard," formerly also met with in the "soft" form.
"Hard" only.	{	Mexican, or Vera Cruz elemi; probably, from <i>Amaryis elemifera</i> .
		Rio elemi; probably a mixture of different <i>Protium</i> elemis.
		Brazilian Almessegia elemi; probably from <i>Protium heptaphyllum</i> , M., var. <i>Brasiliense</i> , Engl.
		African elemi (Luban Matti); probably from <i>Boswellia Freriana</i> .
	{	East Indian elemi, probably from <i>Canarium zephyrinum</i> .

II. Varieties similar to Elemi—

(a) Those resembling elemi in odour, and most nearly allied thereto—

"Hard" only.	{	East Indian Tacamahac; probably from <i>Calophyllum Inophyllum</i> .
		Bourbon Tacamahac; probably from <i>Calophyllum Tacamahaca</i> .
		Resina anime ¹ from the East and West Indies; also derived from <i>Burseraceæ</i> .

¹ For Anime, see also under Copal. Here, of course, the *Bursera* resin of elemi character is meant and not Courbaril, and the other soft copals usually

(b) Those with an odour resembling incense, and more nearly allied to the latter.

“Hard” only.	{	Cayenne incense ; probably from <i>Icica heptaphylla</i> , etc.
		Gommart gum (also characterised as similar to mastic) ;
		from <i>Bursera gummifera</i> .
		Occuméresin ; from a West African (Gaboon river) <i>Bursera</i> .
		West India Tacamahac ; probably from <i>Icica heptaphylla</i> , etc.

III. Varieties less closely approaching True Elemi in Odour and Appearance—

“Hard” only.	{	Resina Caranna ; probably from <i>Icica caranna</i> .
		Resina Kikekunemalo }
		Resina Hyowæ } from still unknown <i>Burseraceæ</i> .
		Resina Hedwigiaë ; from <i>Hedwigia balsamifera</i> . (See footnote, p. 157.)
		Gum copal ; from <i>Dacryodis hexandra</i> .

According to their colour, the author ranks Manila and Yucatan elemi among the white varieties ; Resina anime and Vera Cruz elemi to the yellow to yellowish red kinds ; whilst the African elemis, Protium elemis, and Tacamahacs, he groups with the grey to greyish black sorts with white-speckled surface of fracture. The more remote members—Res. caranna, Res. kikekunemalo, Res. Hyowæ, and Res. Hedwigiaë, etc., are dark coloured to black.

The author has further observed that Resina Hyowæ is nearly allied to Caranna resin, and the latter to Vera Cruz elemi. Again, whilst West Indian Tacamahac is decidedly allied—already in the aroma—to incense, Bourbon and East Indian Tacamahac more resemble elemi.

Owing to the uncertainty of their origin, it is hardly

termed “anime” in England. The identification of anime resin with Courbaril copal and the statement—frequently put forward in text-books—that *Hymenaea Courbaril* is the parent tree of anime resin is, of course, inaccurate.

possible to lay down any hard and fast limitation for the elemis, the more so because one and the same sort derived from the same kind of tree very often bears different names, according to where it has been gathered. So, for example, certain kinds of Tacamahac resin and cayenne incense are derived from *Icica heptaphylla*, notwithstanding their different names. Such a confusion of nomenclature cannot, of course, be cleared up except by a thorough study of the parent trees *in situ*—if this be at all possible. Although the foregoing list does not exhaust the elemi series—other intermediates to the incense species and other resins being known—the remainder are, however, too remote to deserve inclusion here. With regard to the identification of Bourbon Tacamahac with Caranna resin, and of West Indian anime with Tacamahac, see the summary of analytical data, and also under Caranna resin and Tacamahac.

Adulterants.—Other kinds of elemi.

Analysis.—The commercial varieties of elemi include not merely soft and hard true elemi, but also analogous resins (see above). As a rule, the only difference between the soft and hard kinds is in their content of ethereal oil, which latter imparts a balsamic consistency to the “soft” kinds. Both varieties are largely used in varnish-making, to temper the consistency of the product. Hirschsohn proposed certain general colour reactions, which, however, were opposed by Buri as unreliable. The former worker also determined the solubility of a number of kinds in petroleum ether, and found it range from 30 to 90 per cent. (matter dried at 120° C.).

Von Schmidt and Erban found—

Acid value, d. (S.-Z. d.)	22.1
Ester value (E.-Z.)	2.4
Saponification value, hot (V.-Z. h.)	24.5

Solubility in—

Alcohol	complete.	Petroleum ether	almost compl.
Ether	„	Acetone	complete.
Methyl alcohol	„	Glacial acetic acid	„
Amyl alcohol	„	Chloroform	„
Benzol	„	Carbon di-sulphide	„
		Oil of turpentine	„

A. Kremel found—

	Manila Elemi.	Elemi.
Acid value, d. (S.-Z. d.)	3.0	17.5
Ester value (E.-Z.)	24.2	7.8
Saponification value, hot (V.-Z. h.)	27.2	25.3

The figures obtained by Kremel for (presumably hard) elemi agree with those of von Schmidt and Erban and the author's (see below), who seem also to have had hard Yucatan elemi to work with.

On the other hand, the values given by E. Dieterich and Williams do not at all agree with the above, and they must either have worked with adulterated products or else have used extracts in place of the natural drug. The values obtained by the author confirm those of von Schmidt, Erban, and Kremel, and show the latter are more near the truth.

Williams found—

Acid value, d. (S.-Z. d.)	28.6
Ester value (E.-Z.)	129.0
Saponification value, hot (V.-Z. h.)	157.6
Ash	0.04 per cent.
Moisture	3.50 „

No information is, however, given as to the kind of elemi examined.

E. Dieterich found, for soft elemi—

From extract	Acid value, d. (S.-Z. d.)	26.30
	Ester value (E.-Z.)	103.60
	Saponification value, hot (V.-Z. h.)	129.90

Solubility in—

Chloroform—almost complete			} soluble.
Oil of turpentine	. .	98·32 per cent.	
90 per cent. alcohol	. .	98·26	
Acetic ether	. . .	97·79	
Ether	. . .	91·76	
Benzol	. . .	86·94	
Carbon di-sulphide	. .	63·78	}
Petroleum ether.	. .	44·86	

Whereas Kremel prepared a cold solution and titrated with $\frac{n}{2}$ alkali, Williams dissolved hot, and in that way determined the acid value (direct).

For the saponification value (hot) test, both authors employed heat under a reflux condenser for half an hour, and titrated back with $\frac{n}{2}$ sulphuric acid or $\frac{n}{2}$ hydrochloric acid. E. Dieterich saponified in the same way, but concentrated the liquid so as to expel the alcohol, and then took it up anew. He worked with an alcoholic extract. On the solubility of elemi in β -epi- and di-chlorhydrin (Valenta)—see table in Part I.

Gregor and Bamberger found—

		Gregor.	Bamberger.
Methoxyl value {	. . .	0·0	0·0
(M.-Z.) {	. . .	2·5	0·0

(On the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

Recently, a large amount of analytical data referring to the various elemis has been contributed by the author, including the constants of several rare varieties.

From a number of preliminary experiments it became evident that, unlike many other resins, the elemis do not lend themselves to cold saponification, the values obtained by that method being always, if only slightly, too low. He, therefore, determined the acid value (direct)

by dissolving the sample in alcohol and titrating to redness in presence of phenolphthalein. The saponification value was ascertained by the hot method, the resin being boiled for half an hour with alcoholic $\frac{n}{2}$ potash (as in the usual method); but in all cases—unlike some of the above-named authors—he used the natural product in an unaltered condition, and not in the state of an extract.

It may be again mentioned that the author's values for Manila elemi agree very well with those of von Schmidt, Erban, and Kremel, but not with those of E. Dieterich and Williams, both of whom apparently employed extracts or adulterated samples, their values being tenfold those of the other workers. In other varieties of elemi no values are available for comparison.

With regard to the solubility tests and their results, detailed below, it should be noted that *two* results are generally given, viz. "from-to," indicating the difference in action of the same solvent when used "cold" and "warm." Where no difference could be found, only a single result is given.

The author found—

I. Manila Elemi.

(a) *Soft.*

No. 1.	Loss at 100° C.		16.64 per cent.
	Ash		0.052 "
	Acid value, d. (S.-Z. d.)		18.08 17.77
	Ester value (E.-Z)		7.64 9.91
	Saponification value, h. (V.-Z. h.)	25.72	27.68

Solubility in—

Water		insoluble.
96 per cent. alcohol		almost to completely sol.
Ether		completely soluble.
Acetic ether		almost to completely sol.
Petroleum ether		sparingly soluble.

Benzine	partly to almost completely soluble.
Benzol	completely soluble.
Carbon di-sulphide	„ „
Chloroform	„ „
Acetone	partly to completely sol.
Methyl alcohol	sparingly to partly sol.
Amyl alcohol	completely soluble.
Oil of turpentine	almost to completely sol.
Methylal	partly to completely sol.
Acetic anhydride	very slightly soluble.
Chloral hydrate (60 per cent.)	sparingly soluble.
Do. (80 „)	partly to completely sol.
Acetic acid	„ „
Hydrochloric acid	sparingly sol. (rose red).
Sulphuric acid	almost completely soluble (red-brown).
Ammonia	insoluble.
Caustic potash	insoluble.
No. 2. Loss at 100° C.	11·71 per cent.
Ash	0·023 „
Acid value, d. (S.-Z. d.)	24·48 24·14
Ester value (E.-Z.)	25·45 25·84
Saponification value, h. (V.-Z. h.)	49·93 49·98
Solubility, same as No. 1.	
No. 3. Loss at 100° C.	17·71 per cent.
Ash	0·14 „
Acid value, d. (S.-Z. d.)	17·87 17·97
Ester value (E.-Z.)	8·11 7·72
Saponification value, h. (V.-Z. h.)	25·92 25·69
Solubility, same as No. 1.	
No. 4. Loss at 100° C.	15·14 per cent.
Ash	0·10 „
Acid value, d. (S.-Z. d.)	19·05 19·46
Ester value (E.-Z.)	6·15 6·03
Saponification value, h. (V.-Z. h.)	25·20 25·49
Solubility, same as No. 1.	

No. 5. Loss at 100° C.	.	.	.	19.29 per cent.
Ash	.	.	.	0.03 „
Acid value, d. (S.-Z. d.)	.	.	18.68	18.73
Ester value (E.-Z.)	.	.	6.70	7.71
Saponification value, h. (V.-Z. h.)	.	.	25.38	26.44
Solubility, same as No. 1.				

(b) *Hard.*

No. 6. Loss at 100° C.	.	.	.	8.46 per cent.
Ash	.	.	.	0.93 „
Acid value, d. (S.-Z. d.)	.	.	18.02	18.07
Ester value (E.-Z.)	.	.	26.99	24.40
Saponification value, h. (V.-Z. h.)	.	.	45.01	42.47

Solubility in—

Water	.	.	.	insoluble.
Alcohol (96 per cent.)	.	.	.	almost completely soluble.
Ether	.	.	.	partly soluble.
Acetic ether	.	.	.	almost to completely sol.
Petroleum ether	.	.	.	sparingly soluble.
Benzine	.	.	.	partly soluble.
Benzol	.	.	.	almost completely soluble.
Carbon di-sulphide	.	.	.	partly to almost completely soluble.
Chloroform	.	.	.	almost completely soluble.
Acetone	.	.	.	partly soluble.
Methyl alcohol	.	.	.	almost completely soluble.
Amyl alcohol	.	.	.	partly to almost completely soluble.
Oil of turpentine	.	.	.	partly soluble.
Acetic anhydride	.	.	.	„
Methylal	.	.	.	„
Chloral hydrate (60 per cent.)	.	.	.	„
Do. (80 „)	.	.	.	„
Acetic acid	.	.	.	sparingly soluble.
Hydrochloric acid	.	.	.	insoluble.
Sulphuric acid	.	.	.	almost completely soluble (red-brown).
Ammonia	.	.	.	slightly soluble.
Caustic potash	.	.	.	„

No. 7.	Loss at 100° C.	. . .	6.74	per cent.
	Ash	3.43	„
	Acid value, d. (S.-Z. d.)	. . .	21.84	24.33
	Ester value (E.-Z.)	. . .	45.80	45.72
	Saponification value, h. (V.-Z. h.)	. . .	67.64	70.05
	Solubility, same as No. 6.			

No. 8.	Loss at 100° C.	. . .	10.25	per cent.
	Ash	0.06	„
	Acid value, d. (S.-Z. d.)	. . .	5.71	4.49
	Ester value (E.-Z.)	. . .	34.96	27.05
	Saponification value, h. (V.-Z. h.)	. . .	40.67	31.54
	Solubility, same as No. 6.			

II. Yucatan Elemi.

(a) *Soft.*

No. 9.	Loss at 100° C.	. . .	17.07	per cent.
	Ash	0.03	„
	Acid value, d. (S.-Z. d.)	. . .	22.50	22.29
	Ester value (E.-Z.)	. . .	5.68	9.81
	Saponification value, h. (V.-Z. h.)	. . .	28.18	32.10

Solubility in—

Water	insoluble.
Alcohol (96 per cent.)	. . .	almost completely soluble.
Ether	„ „
Acetic ether	completely soluble.
Petroleum ether	slightly soluble.
Benzine	slightly to almost completely soluble.
Benzol	completely soluble.
Carbon di-sulphide	„ „
Chloroform	„ „
Acetone	„ „
Methyl alcohol	partly to completely sol.
Amyl alcohol	almost completely soluble.
Oil of turpentine	„ „
Acetic anhydride	partly to completely sol.
Methylal.	almost completely soluble.

Chloral hydrate (60 per cent.)	.	.	.	imperfectly soluble.
Do. (80 ")	.	.	.	" "
Acetic acid	.	.	.	partly soluble.
Hydrochloric acid	.	.	.	almost insoluble.
Sulphuric acid	.	.	.	completely sol. (dark red)
Ammonia	.	.	.	insoluble.
Caustic potash	.	.	.	"

(b) Hard.

No. 10. Loss at 100° C.	.	.	.	17·86 per cent.
Ash	.	.	.	0·39 "
Acid value, d. (S.-Z. d.)	.	.	.	1·16 1·70
Ester value (E.-Z.)	.	.	.	35·42 36·36
Saponification value, h. (V.-Z. h.)	.	.	.	36·58 38·06
Solubility, same as No. 9.				

III. Vera Cruz Elemi.

No. 11. Loss at 100° C.	.	.	.	5·02 per cent.
Ash	.	.	.	0·24 "
Acid value, d. (S.-Z. d.)	.	.	.	5·98 5·64 11·72
Ester value (E.-Z.)	.	.	.	40·29 28·34 37·32
Saponification value, h. (V.-Z. h.)	.	.	.	46·27 33·98 49·04

Solubility in—

Water	.	.	.	insoluble
Alcohol (96 per cent.)	.	.	.	partly to almost completely soluble.
Ether	.	.	.	completely soluble.
Acetic ether	.	.	.	partly to almost completely soluble.
Petroleum ether	.	.	.	insol. to very slightly sol.
Benzine	.	.	.	" "
Benzol	.	.	.	almost completely soluble.
Carbon di-sulphide	.	.	.	" "
Chloroform	.	.	.	" "
Acetone	.	.	.	partly to almost completely soluble.
Methyl alcohol	.	.	.	sparingly soluble.
Amyl alcohol	.	.	.	almost completely soluble.

Oil of turpentine	slightly to partly soluble.
Acetic anhydride	„ „ „
Methylal	„ „ „
Chloral hydrate (60 per cent.)	„ „ „
Do. (80 „)	partly soluble.
Acetic acid	„
Hydrochloric acid	almost insoluble.
Sulphuric acid	almost completely soluble.
Ammonia	slightly soluble.
Caustic potash	„
No. 12. Loss at 100° C. . . .	4.90 per cent.
Ash	0.06 „
Acid value, d. (S.-Z. d.)	36.47 34.85 36.79
Ester value (E.-Z.)	49.78 38.15 42.10
Saponification value, h. (V.-Z. h.)	86.25 73.00 78.89
Solubility, same as No. 11.	

IV. African Elemi (Luban Matti).

No. 13. Loss at 100° C. . . .	6.06 per cent.
Ash	3.52 „
Acid value, d. (S.-Z. d.)	13.29 14.23
Ester value (E.-Z.)	47.87 45.18
Saponification value, h. (V.-Z. h.)	61.16 59.41

Solubility in—

Water	insoluble.
Alcohol (96 per cent.)	almost completely soluble.
Ether	„ „
Acetic ether	slightly to almost completely soluble.
Petroleum ether	slightly soluble.
Benzine	„
Benzol	almost completely soluble.
Carbon di-sulphide	partly to almost completely soluble.
Chloroform	almost completely soluble.
Acetone	slightly to partly soluble.

Methyl alcohol	.	.	.	slightly to partly soluble.
Amyl alcohol	.	.	.	partly soluble.
Oil of turpentine	.	.	.	almost completely soluble.
Acetic anhydride	.	.	.	partly to almost completely soluble.
Methylal	.	.	.	partly to almost completely soluble.
Chloral hydrate (60 per cent.)	.	.	.	slightly soluble.
Do. (80 „)	.	.	.	partly soluble.
Acetic acid	.	.	.	slightly soluble.
Hydrochloric acid	.	.	.	very slightly soluble.
Sulphuric acid	.	.	.	almost completely soluble.
Ammonia	.	.	.	slightly soluble.
Caustic potash	.	.	.	„

No. 14. Loss at 100° C.	.	.	.	1·86 per cent.
Ash	.	.	.	0·63 „
Acid value, d. (S.-Z. d.)	.	.	.	14·59 15·09
Ester value (E.-Z.)	.	.	.	15·74 15·56
Saponification value, h. (V.-Z. h.)	.	.	.	30·33 30·65

Solubility, same as No. 13.

No. 15. Loss at 100° C.	.	.	.	5·89 per cent.
Ash	.	.	.	1·19 „
Acid value, d. (S.-Z. d.)	.	.	.	35·80 37·33
Ester value (E.-Z.)	.	.	.	54·14 55·71
Saponification value, h. (V.-Z. h.)	.	.	.	89·94 93·04

Solubility, same as No. 13.

V. Indian Elemi.

No. 16. Loss at 100° C.	.	.	.	3·38 per cent.
Ash	.	.	.	0·16 „
Acid value, d. (S.-Z. d.)	.	.	.	32·46 35·77
Ester value (E.-Z.)	.	.	.	54·48 64·40
Saponification value, h. (V.-Z. h.)	.	.	.	86·94 100·17

Owing to lack of material, the solubility could not be determined.

VI. Protium (Allmessega) Elemi.

No. 17. Loss at 100° C.	2.87 %	1.66 %
Ash	0.32 %	0.44 %
In 96 per cent. alcohol	insoluble	3.65 %
Acid value, d. (S.-Z. d.)	38.45	39.41
Ester value (E.-Z.)	35.82	34.23
Saponification value, h. (V.-Z. h.)	74.27	73.64

Solubility in—

Water	insoluble.
Alcohol (96 per cent.)	almost to completely sol.
Ether	completely soluble.
Acetic ether	partly to almost completely soluble.
Petroleum ether	slightly to partly soluble.
Benzine	very slightly soluble.
Benzol	almost completely soluble.
Carbon di-sulphide	” ”
Chloroform	completely soluble.
Acetone	partly to completely sol.
Methyl alcohol	partly soluble.
Amyl alcohol	almost completely soluble.
Oil of turpentine	partly soluble.
Acetic anhydride	partly to almost completely soluble.
Methylal	slightly to partly soluble.
Chloral hydrate (60 per cent.)	partly soluble.
Do. (80 ”)	mostly soluble.
Acetic acid	partly to almost completely soluble.
Hydrochloric acid	almost insoluble.
Sulphuric acid	almost completely soluble.
Ammonia	slightly soluble.
Caustic potash	,,

VII. Resina Gommart.

No. 18. Loss at 100° C.	1.69 %	
Ash	0.14 %	0.15 %
Acid value, d. (S.-Z. d.)	46.41	47.42
Ester value (E.-Z.)	53.76	51.92
Saponification value, h. (V.-Z. h.)	100.17	99.34

VIII. Anime.

	Acid Value, d. (S.-Z. d.).	Ester Value (E.-Z.).	Saponification Value, h. (V.-Z. h.).
No. 19. East India Anime .	{ 29·69 30·64	29·77 38·67	59·46 69·31
No. 20. West India Anime .	{ 45·36 47·20	113·93 102·39	159·29 149·59

IX. Caranna Resin.

No. 21—	I.	II.
Acid value, d. (S.-Z. d.) . . .	79·37	79·37
Ester Value (E.-Z.) . . .	110·48	111·84
Saponification value, h. (V.-Z. h.)	189·85	191·21

X. Tacamahac Resins.

	Acid Value, d. (S.-Z. d.).	Ester Value (E.-Z.).	Saponification Value, h. (V.-Z. h.).
No. 22. Bourbon Tacamahac .	{ 38·10 39·56	68·22 78·47	106·32 118·03
No. 23. West Indian Tacamahac	{ 28·40 22·71	68·43 75·88	96·83 98·59
No. 24. Do. do.	{ 20·39 27·75	77·33 95·15	97·72 122·90
No. 25. East Indian do.	{ 32·99 34·43	38·81 36·57	71·80 71·00
No. 26. Do. do.	{ 21·41 21·37	32·67 37·58	58·04 58·95
No. 27. Do. do.	{ 22·20 22·60	60·90 66·31	83·10 88·91

In conclusion, the following values were furnished by a Brazilian resin of the elemi type, known as "Almiscar," sent to the author by a friend:—

Loss at 100° C.	6.74 per cent.
Ash	0.54 „
Acid value, d. (S.-Z. d.)	.	.	.	25.35	22.48 26.39
Ester value (E.-Z.)	.	.	.	51.38	30.51 36.45
Saponification value, h. (V.-Z. h.).	.	.	.	76.73	52.99 62.84

results which confirm the impression produced by the appearance and odour of the specimen, to the effect that it is allied to elemi.

From the foregoing series of results it is evident that the soft elemis differ, in the first place, from the hard kinds in their higher percentage of loss at 100° C. In certain cases the soft kinds also exhibit higher acid values, from which it may be concluded that the acid substances are present in the ethereal oil, or that the acid bodies are dispersed in some way during the desiccation of the resins and their conversion into the hard form. These observations, however, could not be confirmed throughout. In all kinds the percentage of ash is very low, and the few instances where 3 per cent. and over was found are probably specimens contaminated by accidental mechanical impurities. One per cent. of ash is the highest permissible limit for good elemi. As regards solubility, all the varieties may be termed relatively soluble; ether being a particularly good solvent throughout, then alcohol, chloroform, carbon di-sulphide, benzol, and 80 per cent. chloral hydrate solution. Benzine and petroleum ether are the least effective solvents.

In respect of constants, the true elemis show comparatively low acid and saponification values; this applies to Manila elemi in particular. The scanty solubility of all elemis in ammonia and alkali is in itself an indication that no great amounts of acid or ester-like constituents are present. The neutral "resenes" apparently predominate. This may also explain why elemi, as relatively resistant towards

reagents, is largely used for tempering varnishes. As a general rule the acid, ester, and saponification values seem to increase the more remote the specimen is from the *Καθ' ἑξοχὴν* elemi—Manila elemi—on the list drawn up by the author and already detailed. This is seen most clearly in the case of Anime and Caranna resin, and still more so with Gommart. Protium (Almessega) elemi is more closely allied to the African and Indian kinds than to Manila elemi. The author was unable to confirm Hirschsohn's assumption that Bourbon Tacamahac is identical with Caranna resin (*q.v.*).

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28. Guaiacum Resin.

Resina Guajaci.

Origin and Habitat.—*Guajacum officinale* (Zygophyllæ). Tropical America.

Chemical Constituents.—Guaiacum resin ($C_{20}H_{23}O_3OH$); guaiaconic acid ($C_{20}H_{22}O_3(OH)_2$); guaiacic acid ($C_{21}H_{19}O_4(OH)_3$) (Hadelich's β -resin); guaiacol and guaiacum yellow ($C_{20}H_{20}O_7$). (Döbner and Lücker.)

According to Herzig and Schiff, guaiacum resin contains two HO groups, and two OCH_3 groups, whereas Döbner and Lücker found only one hydroxyl group. The difference in these results may be principally due to variation in the methods employed for acetylising.

General Properties and Commercial Varieties.—

Guaiacum in massa forms a dark green to brownish black amorphous mass, dusty on the surface, of vitreous conchoid fracture, transparent in thin splinters, and frequently contaminated with fragments of wood and bark. When chewed, the mass softens and has a strongly irritant taste. The resin melts at about 85° C., and resembles benzoin in odour. Its alcoholic solution is turned a beautiful blue or green by oxidising agents. *Amber guaiacum* is merely a very pure kind of guaiacum, and has nothing in common with amber. The variety known as *alcohole depuratum* and *in lacrymis* is preferable to the *in massa* kind, on account of its greater purity, but is rarely met with in commerce.

Adulterants.—Colophony, and the very similar but yellowish brown resin, *Guajacum peruvianum odoriferum*.

Analysis.—Only two kinds of guaiacum are at present on the market in any quantity—the natural crude, and the purified resin; the variety “guaiacum in tears” is now very rare.

Ward found—

	I.	II.	III.
Ash	2.99	3.34	6.85 per cent.
Soluble in alcohol	96.2	92.9	87.28 „
Soluble in water		3.0–4.66	per cent.

According to Hager the points to be taken in consideration are—

Physical properties.

Solubility in chloroform and ethyl alcohol.

For the detection of colophony in guaiacum the same authority recommends the addition of an excess of caustic potash to the alcoholic solution, the colophony being thrown down as an insoluble resin soap. The Storch-Morawski

reaction for the same purpose has already been described under Colophony.

Hirschsohn found—

		Soluble in Petroleum Ether—	
		Dried at 17° C.	at 120° C.
Guaiacum	<i>in granis</i>	2.35 per cent.	2.00 per cent.
Do.	<i>lacrymis</i>	2.92 „	2.01 „
Do.	<i>massis</i>	2.10 „	1.80 „
Do.	<i>do.</i>	3.03 „	2.40 „
Do.	<i>do.</i>	4.03 „	3.97 „

Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	23-28	44

by the direct method, and rightly limited his experiments to this value; Döbner and Lücker having, as already mentioned, found guaiacum to be free from ester, and to contain only resin acids similar to phenols.

Evans found—

	Insoluble Matter.	Ash in Insoluble Matter.
Resin in blocks, <i>prima</i>	2.99 per cent.	56.2 per cent.
Do. <i>do.</i>	7.66 „	18.0 „
Do. <i>do.</i>	7.89 „	23.1 „
Do. <i>do.</i>	10.00 „	18.7 „
Resin in tears <i>do.</i>	1.54 „	11.5 „
Do. <i>secunda</i>	9.00 „	20.2 „

Rabenau found—

	I.	II.	III.
	%	%	%
Soluble in petroleum ether	0.06	0.02	0.01
Soluble in ether	57.80	73.90	66.90
Insoluble in ether and alcohol	9.90	6.10	12.20
Ash	6.45	4.75	9.75

E. Dieterich found the following percentages of solubility in—

	<i>G. in massa.</i>	<i>Depuratum.</i>	<i>Naturale.</i>	<i>Pulveratum.</i>
90 per cent. alcohol .	75.99	complete.	52.28–79.24	95.18%
Acetic ether . .	75.70	„	49.17–97.22	94.62
Chloroform . .	64.23	„	33.91–89.18	96.72
Ether . . .	69.91	90.66	22.93–80.56	87.08
Benzol . . .	68.40	89.09	19.39–89.72	69.66
Oil of turpentine .	47.77	59.96	12.23–55.89	41.89
Carbon di-sulphide .	27.81	34.33	12.41–23.69	34.46
Petroleum spirit .	6.69	6.16	1.93–10.06	6.31

The author has worked out the following new method for determining the acid value of guaiacum, and recommends back titration, in preference to the direct process, as a better means of securing a more suitable titration liquid and the complete combination of the resin acids.

(a) *Acid value, ind.* (S.-Z. ind.).—One grm. of resin is suffused with 10 c.c. of alcoholic $\frac{n}{2}$, and 10 c.c. of aqueous $\frac{n}{2}$ caustic potash, and left for twenty-four hours in a flask fitted with a glass stopper. After adding 500 c.c. of water, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein.

(b) *Ash.*—Two grms. of the drug are incinerated with care.

The values obtained were—

<i>G. in massa</i> , acid value, ind. (S.-Z. ind.) .	89.60–92.50
<i>G. depuratum</i> do. do. .	89.60–97.50
<i>G. in lacrymis</i> do. do. .	72.00–75.60

The commercial grade “in massa” should not contain over 10 per cent. of ash, whilst the “purified” and “in tears” kinds should contain as little as possible. These last two kinds should be almost completely soluble in strong alcohol.

Adulteration with colophony is revealed by the very high acid values then furnished.

For detecting colophony and Peruvian guaiacum (*Guaiacum peruvianum odoriferum*), Hirschsohn recommends bromine solution. The pure resin, dissolved in chloroform, should give with this reagent a blue coloration; adulterated specimens a red coloration. Petroleum ether will extract only 2–3 per cent. (see above) from the pure resin, but up to 42 per cent. from adulterated kinds. (More correctly stated, the adulterated specimens show a very high percentage of matters soluble in petroleum ether. According to E. Dieterich, the pure kinds yield over 3 per cent., some as much as 10 per cent., to this solvent.)

Mauch states that guaiacum is soluble in 60 per cent. and 80 per cent. solutions of chloral hydrate.

The author also determined the acetyl values, and found—

	Acetyl		
	Acid Value. (A.-S.-Z.).	Ester Value. (A.-E.-Z.).	Sapon. Value. (A.-V.-Z.).
<i>G. depuratum</i> .	13·57–14·89	149·33–149·75	163·22–164·22
<i>G. in massa</i> .	45·84–53·15	121·75–139·16	167·59–192·44

Gregor and Bamberger obtained the following methoxyl values—

		I.	II.
Gregor, Methoxyl value (M.-Z.) .		73·8	74·2
Bamberger do. do. .		83·8	84·0

From the above data, it is evident that the variety “in massa” is the poorest, and that “in tears” the best kind of guaiacum, the “purified” grade occupying an intermediate position. All three kinds are distinguishable by their acid value, ash content, and degree of solubility in alcohol.

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29.—Jalapa Resin.

Resina Jalapæ (officinal in Germ. Pharm. III.).

Origin and Habitat.—*Ipomœa Purga*, Hayne (Convolvulaceæ). Mexico.

Chemical Constituents.—Convovulin ($C_{31}H_{50}O_{16}$), insoluble in ether ; also Jalapin = Orizabin ($C_{34}H_{56}O_{16}$), soluble in ether (W. Mayer).

General Properties and Commercial Varieties.—Long, round, dark, or black sticks, with lustrous fracture and dull outside ; practically insoluble in water, but soluble in alcohol and partly so in ether. According to Georgidas, *Convolvulus althæoides* also yields a resin, said to be suitable for replacing the officinal variety. It is contained, to the extent of 6–7 per cent., in the said *Convolvulacea* (Beyrout and vicinity), and contains 25 per cent. of substances soluble in ether.

Adulterants.—Resin from *Fungus Laricis*, colophony, guaiacum resin, aloes, myrrh, resin from Jalapa stalks, Tolu balsam.

Analysis.—A copious literature exists on Jalapa resin, and especially with regard to the nodules from which the resin is artificially obtained by extraction with alcohol. Numerous workers have interested themselves with the percentage content of resin in Jalapa ; and, as the question is an important one, their labours are recorded here.

Trommsdorf found 10·00–11·25 per cent. of resin; Dulk, 12·5 per cent.; Baudimont, 14 per cent.; Bernatzik, 9–12 per cent. Schwabe found at first 14 per cent.; later, only about 7 per cent. of resin, and was the first to confirm the retrogression of the Jalapa nodules in point of resin content. Schacht found 10–12·5 per cent. of resin.

Guibourt found—

I.		II.	III.	
Official Jalapa—		Orizaba Jalapa—	Finger Jalapa—	
Medium.	Young.		Medium.	Young.
17·65	14·68	8·00	7·38	3·91 % resin.

So that in general the younger nodules are poorer in resin than the older ones. Vulpius showed that now they contain not more than 10 per cent.; and Flückiger also confirmed the decrease to this figure, from the former rate of 20 per cent.

Von Ledden-Hulsebosch found that commercial Jalapa powder contains from 7–9·6 per cent., and states that 10 per cent. is scarcely ever attained at present.

E. Dieterich, in his pharmaceutical manual, gives the yield as 12–14 per cent. Bellingrodt placed it at 11·58 per cent.; later, at 11·60 per cent., stating that 10 per cent. could well be laid down as a minimum. Waage found 12 per cent. of resin; Turner and Squibb, less than 10 per cent., viz. 7·32, 9·10, 8·72, 7·82, 6·51, 8·79, and 6·19 per cent. Alcock extracted with amyl alcohol, and also obtained below 10 per cent. Cripps found over 10 per cent. in fourteen kinds, and more than 12 per cent. in seven; he gave the lowest limit as 5 per cent.; the highest, 15 per cent.

That the percentage of resin in Jalapa nodules has decreased in the course of years, and that—as is now

unfortunately the case with nearly every kind of drug—inferior goods are in the market may therefore be regarded as proved. Perhaps this is due to an inferior method of collection, or maybe to some fermentation process that did not occur formerly. For, as shown by E. Dieterich, whereas an unfermented gentian root yields 40 per cent. of extract, fermented root yields only 20 per cent. Such fermentation might occur through the careless piling up of large quantities of the drug.

Bearing the first-named point in mind, the German Pharmacopœia, No. II., went rather too far, and required only 7 per cent. of resin, against which clause both Thoms and Bellingrodt rightly raised objection, and desired to fix 10 per cent. as the minimum; and indeed, in view of the fact that other Pharmacopœias demand 10 and even 12 per cent., the aforesaid minimum of 7 per cent. seems to be decidedly too low. The author can only approve the 10 per cent. proposed by Thoms, since, if traders find the Pharmacopœia so yielding, they are likely to still further lower the standard of their wares, in the expectation that the limits prescribed by the Pharmacopœia will be again reduced.

So far as the examination of Jalapa is concerned, the expensive nature of the drug has caused this to be widely advocated and attempted.

Colophony, extracts, and false Jalapa resins are the main adulterants. Laneau describes an adulterated resin which ceded 90 per cent. to ether, whereas only 2 per cent. is soluble in the case of the pure resin. For the Storch-Morawski reaction for colophony, see the description of that resin. Bernatzik, in his comprehensive treatise on Jalapa, gave a method for detecting false resin, based on the divergent solubility of the two resins in chloroform. Kohl-

mann, however, characterised it as tedious, and proposed to employ the sp. gr. as a distinctive indication, that of the pure resin being 11·46, and of stalk resin, 1·047; and on the basis of this difference he calculated the percentage of both in a mixture. This method seems to the author rather hazardous, since it is clear that the pure resin, which always contains more or less air, cannot have a constant sp. gr. How much the more then is the quantitative calculation a risky procedure! The author's experience shows that the method requires using with great care. (Compare the sp. gr. found by Beckurts and Brüche, given below.)

The former Pharmacopœia Committee advised the ammonia test as a characteristic one, the resin being warmed with ammonia—whereby the convolvulin is converted into convolvulinic acid—and the filtrate treated with an acid, whereupon any colophony present should come down as a flocculent or gelatinous precipitate, the convolvulinic acid not being thrown down from the ammoniacal solution. Later on, however, the committee found that nearly all Jalapa resins, even when pure, give a precipitate with acid, and modified the method so that 2 grms. of resin warmed with 10 grms. of ammonia should furnish a solution that would not gelatinise. The German Pharmacopœia, No. III., prescribes non-gelatinisation with ammonia, and mere turbidity with acetic acid. This latter test is, however, incorrect, there being few if any resins that will give nothing more than turbidity with acid, most of them yielding a precipitate. Further on it is required that the resin shall produce no coloration when ground in a tenfold quantity of water. Unfortunately the ammonia test in its original form has found its way even into the newest text-books, whereas only the modified form, without addition of acid, is acceptable. Hirsch, in his critique on the American Pharmacopœia

states that the matters soluble in ether are precipitated by acid when they have been redissolved in 5 per cent. caustic potash after the evaporation of the ether, whereas the portion insoluble in ether does not come down when treated in the same manner.

In any case, no great reliability can be placed on these qualitative tests, as is shown by the fact that later investigators occupied themselves with quantitative examinations on the usual analytical lines, leaving the aforesaid tests in the background.

We are indebted, for the first quantitative values, to Kremel, who found—

	Acid Value, d. (S.-Z. d.).	Ester Value (E.-Z.).	Sapon. Value, h. (V.-Z. h.).
Jalapin	14.7	172.9	187.6
Jalapa resin	12.9	119.8	132.7
Do.	12.1	120.7	132.8

Kremel stated that the one Jalapa resin was prepared by himself, the other being a commercial product. Concordance in the values furnished by two resins of entirely different origin indicates that the method employed is the correct one. An addition of colophony would give a considerably augmented acid value.

On the basis of a considerable number of specimens examined, Beckurts and Brüche formed the conclusion that the sp. gr., solubility in alcohol, and the acid, ester, and saponification values are suitable for determining the worth of Jalapa resin, and for the detection of adulteration. Unfortunately they did not subject any adulterated specimens to examination in this manner: at least they do not say anything about this point.

They found—

	Sp. gr.	Acid Value, d. (S.-Z. d.).	Ester Value (E.-Z.).	Saponification Value, h. (V.-Z. h.).
1.	1.143	15.0	110	125
2.	1.147	13.0	121	134
3.	1.150	18.0	111	129
4.	1.151	27.0	109	136
5.	1.149	11.0	118	129
6.	1.149	20.0	113	133
7.	1.149	14.0	126	140

The percentage soluble in (alcohol free) chloroform should not exceed 6 per cent., as was also laid down by Hager.

The above values agree well with those of Kremel, thus showing that the characteristic values in question are of use in testing Jalapa resin.

According to the *Chemist and Druggist*, Sage examined nodules that had been stored for twenty-eight years, but found them little richer in active constituents than freshly collected specimens. He obtained 11.34 per cent. of total resin, only 7.5 per cent. of which was soluble in ether (0.85 per cent. soluble, and 10.49 per cent. insoluble in ether).

Hooper attributes the divergent resin content of the nodules to the character of the soil (especially in respect of phosphates).

The author has reported on the quantitative examination of pure Jalapa resins prepared by himself, and also of adulterated specimens, as well as on the interesting results obtained by W. Hampe in the Helfenberg laboratory, showing the influence exercised by additions of colophony, guaiacum, and gallipot on the normal values given by Jalapa resin.

The method adopted was as follows:—

(a) *Acid value, direct* (S.-Z. d.)—One half-grm. of *Resina*

Jalapæ is dissolved in 50 c.c. of ethyl alcohol and titrated with alcoholic $\frac{n}{2}$ potash and phenolphthalein, preferably in a high measuring cylinder.

(b) *Saponification value, hot* (V.-Z. h.)—One half-grm. is dissolved in 50 c.c. of alcohol, treated with 25 c.c. of alcohol $\frac{n}{2}$ caustic potash, and heated for an hour on the steam bath. After cooling in a loosely closed vessel, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The number of c.c. of alcoholic potash consumed per 1 grm. of resin, multiplied by 28.08, gives the saponification value.

This is the same ("usual") method as furnished Kremel the much lower values already cited.

The same method applied to two resins prepared by the author from *Tubera Jalapæ* gave very concordant results—

		Referred to dry substance.			
I. Res. Jal.		II. Res. Jal.		I. Res. Jal.	
ipse parat.		ipse parat.		with 3.4 %	
				loss in drying.	
Acid value, {		26.58		27.30	
d. (S.-Z. d.) {		27.13		27.30	
Sapon. val., {		244.72		234.04	
h. (V.-Z. h.) {		—		253.32	
				—	
				246.30	

Since these figures do not agree with those of the authors cited above, further experience is necessary to decide which are the more correct. Those now given may at anyrate lay claim to full worth, having been obtained from perfectly pure resins prepared at first-hand.

In order to determine the value of the method itself, it was then applied to purposely adulterated Jalapa resins. Three of the most customary adulterants were added, in

not too large proportion, to the above-mentioned II. Res. Jalapæ; and the following results were obtained:—

Resina Jalapæ ipse parat.	The same with					
	10 % Colo- phony.	20 % Colo- phony.	10 % Guaia- cum.	20 % Guaia- cum.	10 % Galli- pot.	20 % Galli- pot.
Acid value, d. {	27·30	39·08	54·07	32·13	39·62	42·29
(S.-Z. d.) {	27·30	39·08	53·54	29·45	39·08	41·76
Saponification {	234·04	321·84	221·76	221·76	202·16	221·76
value, h. (V.-Z. h.) {	234·04	231·84	223·44	221·20	204·96	221·76
						211·12

Thus colophony, even in small amount, largely increases the acid value; Resina guajaci considerably depresses the saponification value; and gallipot, like colophony, tends to raise the acid value. The influences exercised by even small proportions of these adulterants are appreciable, and would naturally be more so were the amounts greater.

The same mixtures were examined by the test prescribed by the Germ. Pharm. III., with the result that no objection would be taken, on the basis of this test, to such of them as contained 10 per cent. of adulterants, or even that containing 20 per cent. of guaiacum. The defect of this method lies in the circumstance that the added resins also are soluble in ammonia, and that a portion of the Jalapa resin is also precipitated from the ammoniacal solution.

The following results were obtained in the examination of a commercial specimen of Jalapa resin which had been purposely adulterated with powdered gum and also with colophony:—

Resina Jalapæ pulv. adulterated with		
Gum.	Gum and 25 % of Colophony.	Gum and 50 % of Colophony.
Acid value, {	18·82	53·15
d. (S.-Z. d.) {	19·37	53·70
Sapon. val., {	154·50	164·60
h. (V.-Z. h.) {	155·20	164·60
		—

These figures show that the method is very well adapted for the detection of adulterants, an assumption which agrees with the experience of the authors already cited.

The carbonyl value also has been determined by Kitt, who found it = 1.02.

Gregor and Bamberger applied the methoxyl value test with negative results.

(For the value of these determinations, see *Chem. Rev.*, 1898, No. 10.)

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30. Kino.

Origin and Habitat.—Ordinary Amboyna Malabar kino is obtained from *Pterocarpus Marsupium* (Papilionaceæ); Bengal kino from certain species of *Butea* (Leguminosæ); the Australian varieties from species of *Eucalyptus* (Myrtaceæ); and *Angophora*; Jamaica or West Indian kino from *Coccoloba uvifera* (Polygonææ); whilst African kino comes from *Pterocarpus erinaceus*. Similar sap-products are furnished by numerous other trees, such as species of *Angophora*, *Ceratopetalum apetalum* and *gummiferum*, and also by species of *Millatia* (Leguminosæ). According to Schaer, Mexican dragon's-blood from *Croton Draco*, and dragon's-

blood from Columbia and Venezuela are similar to Malabar kino, a remark which also applies to Kât-Jadikai, a kino from *Myrristica Malabaricum*.

Liquid kino is derived from *Angophora intermedia*, Queensland. French (south) cultivated kino comes from *Eucalyptus leucoxylon* and *E. viminalis*. Kino from Colombo, Bangley Creek, and Eastwood is furnished by *Angophora cordifolia*, *subvelutina*, *woodsiana*, *lanceolata*, and *intermedia*. Kino from Botany and the Blue Mountains, comes from *A. lanceolata*, not, as erroneously assumed, from *Eucalyptus maculata* (Maiden). Malabar, Africa, Australia, Jamaica, and Southern France.

Chemical Constituents.—Malabar kino contains—kino-tannic acid, 85 per cent.; ash, 13 per cent.; kino red, and pyrocatechuic acid. The varieties from *Pterocarpus erinaceus* contain pyrocatechin (Flückiger). Kât-Jadikai from *Myrristicum Malabaricum* contains small quantities of crystalline calcium tartrate, but in other respects has the same composition as Malabar kino. Whereas kino from *Pterocarpus* contains pyrocatechuic acid, the varieties from *Eucalyptus* also contain a small amount of gallic acid (Kremel). The latter also generally contain gum, some indeed, like the kino from *Eucalyptus gigantea*, containing that substance alone.

General Properties and Commercial Varieties.—Nearly all varieties of kino, from whatever source—Malabar kino (the ordinary commercial article), Australian kinos from *Eucalyptus* and *Angophora*, as well as other kinds—form pale to dark red masses, or granules, with a very astringent taste and imparting a red coloration to the saliva; they are soluble in hot water, alkalis, and, to some extent, in alcohol, and are more or less contaminated with vegetable detritus. Australian *eucalyptus* kinos are in the form of almost black, vitreous tears, which swell up to a gelatinous

mass in water and in alcohol. "Creek gum," from *Eucalyptus rostrata*, is said to be the best kind.

Bengal kino, from species of *Butea*, are black, brittle tears, almost completely soluble in water. This kino, from the bark of *Butea frondosa*, should not be confounded with the stick lac (see Shellac) from the same tree.

Jamaica kino forms small, blackish brown, brittle tears, or masses, with a lustrous fracture. African kino, as also the kinos from species of *Angophora* and *Ceratopetalum*, those from Colombo, Bangley Creek, Eastwood, Botany, Blue Mountains, and liquid kino from Queensland, are practically no longer met with in commerce, and are of merely local importance. The allied varieties of dragon's-blood, from Mexico, Columbia, and Venezuela, are also no longer in the market.

The Hartwich method for differentiating the varieties of kino from species of eucalyptus, is referred to later on (see Analysis).

Adulterants—Other varieties of kino.

Analysis.—**I. Malabar Kino.**—True analytical data are almost entirely lacking, and therefore the solubility and other properties must be called in aid. Kino is slightly soluble in cold water, more so in warm water, alkalis, or alcohol, the solutions in the last named having a ready tendency to gelatinise. Ferric sulphate solution gives a green coloration after awhile, the colour changing to violet on the addition of alkali carbonates or acetates. Ferric chloride gives a green precipitate, which turns purple-red in presence of alkalis; and dilute mineral acids produce a flocculent precipitate.

Will and Brauch examined the effect produced on Malabar kino by different methods of drying, and subjected

the sap of *Pterocarpus Marsupium* to different preparatory processes, viz. :—

No. 1, boiling, followed by drying; an operation that lasted several weeks.

No. 2, boiling, followed by drying on the steam bath, which only took about four hours.

No. 3, spreading out in thin layers to dry in the sun (twelve hours).

No. 4, spreading out in thin layers, and drying for twenty-four hours in the shade.

No. 5 was a specimen of Malabar kino prepared from unboiled sap.

No. 6, one from boiled sap.

The following results were obtained :—

No. 1 consisted of small, angular, red-brown fragments, which furnished a terra-cotta powder, and was soluble to the extent of 57 per cent. in water, 78 per cent. in rectified alcohol, and 78·5 per cent. in pure alcohol. It contained 39·33 per cent. of tannic acid, and 1·13 per cent. of ash.

No. 2 formed small, angular, very friable, red-brown, lumps, with clear surface and translucent corners. Water dissolves 77·4 per cent., rectified alcohol 85 per cent., pure alcohol 84 per cent., tannin 49·17 per cent., ash 1·1 per cent.

No. 3 was in small regular, reddish black lumps, soluble to the extent of 79·6 per cent. in water, 81 per cent. in rectified alcohol, 86·5 per cent. in pure alcohol, and contained 49·76 per cent. of tannin and 1·0 of ash.

No. 4, thin transparent lamellæ of a brilliant red colour, soluble to the amount of 77·6 per cent. in water, 84 per

cent. in rectified alcohol, 83·5 per cent. in pure alcohol, and containing 45·3 per cent. of tannin, and 1·3 per cent. of ash.

No. 5, small angular lumps, and thin, ruby red, transparent lamellæ. Solubility, in water 77 per cent., in rectified alcohol 83 per cent., in pure alcohol 85 per cent. Tannin content 55·13 per cent., ash 0·8 per cent.

No. 6 consisted of angular fragments of various sizes, dark brown in colour, soluble to the extent of 58 per cent. in water, 77 per cent. in rectified alcohol, 79·5 per cent. in pure alcohol, and containing 41·12 per cent. of tannin and 0·7 per cent. of ash.

From these data it is evident that the varieties dried in the sun or by artificial heat are fairly alike, and that it is not advantageous to boil the sap before drying. The Zambesi kino examined by the same authors proved to be an inferior article, and had, moreover, been badly prepared.

C. B. Breidenbach found the maximum percentage of ash in various sorts of kino to be 2·8 per cent., the minimum being 1·2 per cent.

Solubility in—

Ether	0·29–0·81 per cent.
Absolute alcohol	94·00–99·00 „
95 per cent. alcohol	90·00–97·40 „
Water	10·00–17·90 „

According to Christy & Co., the true Malabar kino almost entirely disappeared from the European market for a number of years, but is now available in sufficient quantity once more. They examined a series of commercial samples—only one of which (No. 6) was pure—and obtained the following results :—

Appearance.	Ash %	Solubility in water.	Solubility in rectified alcohol.	Tannin % (Löwen- thal).
1. Black ; reddish brown when powdered	4 % grey	The greater part soluble ; dark red	Less than half	34.4 %
2. Violet-black	2.8 % grey	Almost com- plete ; pale-red solution	Three- fourths	39.9 %
3. Garnet red drops, adhering to bark	6 % grey	Greater part sol- uble ; port wine colour	Gelatinised	28.0 %
4. Black ; red when powdered	3.4 % white	Almost com- plete ; dark port wine colour	—	26.2 %
5. Deep black ; brown when powdered	7.0 % grey	Less than half ; port wine col- our	—	14.2 %
6. Pure kino, garnet red	1.7 % white	About three- fourths ; pale red solution	almost complete	52.0 %

At the present time, Malabar Amboyna kino is the only kind used for medicinal purposes, *e.g.* as tincture. The other sorts are almost exclusively devoted to technical uses: dyeing and tanning. Certain kinds of dragon's-blood (see above), and cultivated (eucalyptus) kinos from the south of France, are very similar to Malabar kino.

Caesar & Loretz report the result of their researches as follows:—

“ Within the last few years we have given more particular attention to the testing of these drugs, and have found, in the first place, that the several commercial varieties differ from one another in a remarkable degree, and also that the prices quoted for some are often out of all proper proportion to their actual value and qualitative composition. The points that should determine the value

of any kino are: percentage of tannin, solubility in water and alcohol, and the amount of residue left after combustion, rather than the—often entirely arbitrary—classification according to centres of production.

“To afford a better insight into the matter we subjoin the results of our last year’s testings:—

	1	2	3	4	5	6	7	8	9
	%	%	%	%	%	%	%	%	%
Soluble in 90 % alcohol .	97·94	97·60	97·24	96·67	96·74	97·70	93·54	97·43	89·67
Soluble in water . .	86·00	97·07	96·48	97·57	95·86	91·43	89·07	96·99	90·89
Tannin . .	60·38	59·31	53·17	47·60	58·51	58·32	55·20	52·73	43·82
Ash . . .	2·79	1·26	0·77	1·11	1·58	0·53	0·91	0·80	6·23
Moisture .	12·24	17·57	17·11	16·91	17·24	17·72	8·51	10·87	12·18

“Nos. 1–8 are best commercial grades from *Pterocarpus Marsupium* and *P. erinaceus*; No. 9, a doubtful African kino, the aqueous and alcoholic solutions of which were remarkably pale, turbid, and almost unfilterable. The tannin determinations were made in the usual manner, with lead acetate.”

II. Australian Kinos.—Maiden gives the following data for new Australian kino from *Millettia megasperma* (the first occurrence of kino in Australian *Leguminosæ*):—

Tannic acid	78·00 per cent.
Moisture	20·00 „
Ash	0·8 „
Insoluble	0·9 „

and states that almost all kinos furnish a turbid solution with water. Nearly all eucalyptus kinos are partly soluble in alcohol; only that from *Eucalyptus gigantea* contains so much gum that it is quite insoluble in alcohol. Maiden found for liquid kino from *Angophora intermedia* (Queensland)—

Sp. gr.	1·022
Tannic acid	3·048 per cent.
Solution in ether . . .	0·150 „

The ethereal extract consisted of catechin and resin.

According to Kremel, all varieties of eucalyptus kino contain gallic acid in addition to protocatechuic acid.

Wiesner found in eucalyptus kino 15–17 per cent. of moisture, traces of ash, gum in nearly all (that from *Eucalyptus gigantea* consists solely of gum), catechin, and pyrocatechin ; sp. gr. 1·11–1·14, the samples sinking in water. The solutions lather, and give with ferric chloride a black-green precipitate, with sulphuric acid a pale red precipitate.

Heckel & Schlagdenhaufen confirmed the similarity between Malabar kino and that from *Eucalyptus leucoxydon* and *E. viminalis* (Southern France), which furnished them with the following values :—

Kino from—

Eucalyptus leucoxydon.		Eucalyptus viminalis.	
Moisture	18·94	7·083	
Salts	1·32	—	
Tannin and catechin . .	74·95	92·667	
Gum	2·74	—	
Ligneous detritus . .	1·51	—	
Loss	0·54	—	
Ash	---	0·250	
	<hr/> 100·00	<hr/> 100·000	

Hartwich mentions the following points in connection with the differentiation of the eucalyptus kinos and principal Australian varieties generally :—

(a) The kinos (ruby kinos) from the following species are completely soluble in water and alcohol :—

Eucalyptus amygdalina, Lab.; *E. eugenioides*, Sieber.; *E. hæmastoma*, Smith; *E. macrorhyncha*, F. v. M.; *E. pilularis*, Smith; *E. piperita*, Smith; *E. Sieberiana*, F. v. M.; *E. stellulata*, Sieber; *E. melliodora*, E. Cuom.; *E. obliqua*, L'Hérit.

(b) The kinos from the following species are only partly soluble in alcohol, the residue, consisting of gum, being almost completely soluble in water:—

E. leucoxyylon, F. v. M.; *E. paniculata*, Sm.; *E. resinifera*, Sm.; *E. robusta*, Sm.; *E. saligna*, Sm.; *E. siderophloia*, Benth.

(c) Those furnished by the following species give with alcohol a turbid solution, yellow or orange-brown in colour:—

E. goniocalyx, F. v. M.; *E. hemiphloia*, F. v. M.; *E. rostrata*, Schl.; *E. punctata*, DC.; *E. odorata*, Behr.; *E. Gunii*, Hook; *E. Stuartina*, F. v. M.; *E. viminalis*, Labill.; *E. terminalis*, F. v. M.; *E. corymbosa*, Sm.; *E. microcorys*, F. v. M.; *E. maculata*, Hook.

III. African and West Indian (Jamaica) Kino.—

According to Francis, both Jamaica kino and kino from *Pterocarpus erinaceus* furnish tinctures less stable and more readily gelatinising than Malabar kino. Thoms also examined a kino from *P. erinaceus*, and reports as follows:—

“This is derived from *Pterocarpus erinaceus*, Poir., a tree denominated “Mninga” or “Mininga” in the Suaheli dialect. The sample consists of small, angular, friable lumps of a dark red colour, clear and transparent in thin fragments. It is completely soluble in four parts of hot water, furnishing a tart solution of acid reaction. The cold-prepared aqueous solution is turned violet by ferrous sulphate in presence of well water, or red by caustic soda. Lime water gives a brown precipitate, and the kino-tannic acid is converted into the characteristic kino red by prolonged boiling. Copious precipitates are produced in the aqueous solution by a number of metallic salts. The drug is moderately soluble, to a red

solution, in alcohol. The residue left on incineration is a pure white ash (0·78 per cent.). Attempts to prepare crystalline chinoine from the small sample were unsuccessful. The examination shows that Kilossa kino presents all the physical and chemical characteristics of true kino. The low percentage (0·78) of ash (Flückiger gives about 6 per cent.) in particular stamps it as a very good commercial grade."

IV. Bengal (*Butea*¹) Kino.—Two kinds are used in the producing districts.

Flückiger distinguishes—one variety consisting of flat lumps or rounded granules, dark red, almost black, in colour; and a second, much lighter red, formed of stalactitic lumps. The former contains about fifty per cent. of a substance soluble in alcohol, the remainder being mucus, which in the second variety is so preponderant that the mass is almost completely soluble in water. When treated with caustic potash the kino is converted into a carmine jelly, and ferric chloride turns it green.

According to A. Schmidt, *Butea* kino is less soluble in alcohol than Malabar kino.

According to Schär, Kât-Jadikai from *Myristica Malabarica* differs but very slightly from Malabar kino; it does, however, differ from this and other kinos by containing small quantities of crystalline calcium tartrate.

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¹ Kino from *Butea frondosa* must not be confounded with stick lac (see Shellac) from the same tree.

31. Labdanum.

Resina Ladanum seu. Labdanum.

Origin and Habitat.—*Cistus Cypricus*, *C. Creticus*, *C. ladaniferus* (Cistineæ). Cyprus, Crete, and Southern Europe generally.

Chemical Constituents.—According to Guibourt, Cyprus labdanum *in massa* contains resin, 86 per cent.; ethereal oil, 7 per cent.; wax, earthy matters, and impurities, such as hair, 6 per cent.; extractives, 1 per cent. The so-called labdanum *in tortis* (twist) contains 20 per cent. of resin, 1·9 per cent. of wax, 0·6 per cent. of malic acid, 3·6 per cent. of gum; ferruginous sand, ethereal oil (together 73·9 per cent.) (Pelletier).

General Properties and Commercial Varieties.—Whereas, formerly, labdanum was largely used and highly appreciated as an agreeably scented resin rich in ethereal oil, the only kind now in the market is “Ladanum usu Candia,” a Cretan product, which is very impure and mostly artificial. At one time a very quaint method was employed for collecting this resin, by driving flocks of sheep through the *Cistus* shrubs, and gathering the resin that adhered to the wool. The hairs found by Guibourt (see above) had made their way into the resin in this manner. The grades in the French and German markets are very divergent in character, which implies that the perfectly pure article has vanished and been replaced by artificial products.

Labdanum is in the form of dark brown or black, viscid masses, which soften in the fingers, and exhibit a grey fracture when freshly broken, but soon turning black. It is insoluble in water, but almost completely soluble

in alcohol. The odour, especially of the ethereal oil, is agreeable, like ambergris ; the flavour balsamic and biting.

Labdanum in rods, such as was formerly met with in commerce, seems to have been a very impure kind derived from *Cistus ladaniferus*.

Adulterants.—Artificial products made from colophony, sand, and plumbago. Labdanum was formerly used to adulterate storax.

Analysis.—As already mentioned, labdanum at present enjoys only a very limited application, so that its analysis is relatively unimportant. Nevertheless, the values obtained by the author from different kinds, of French and German origin, may be recorded here, it being remarked that they refer to present day commercial varieties, and that no data on pure labdanum from earlier times are in existence. Hirschsohn, also, regarded as artificial the kinds examined by him in 1877.

The author found—

	Acid Value, d. (S.-Z. d.).	Ester Value. (E.-Z.).	Sapon. Value, h. (V.-Z. h.).
1. Lad. veritable (French commercial grade) . . .	f 90·37 l 91·98	116·10 120·26	206·47 212·24
2. Do. do.	f 98·05 l 98·36	102·06 109·88	200·11 208·24
3. Res. Lad. vera (German commercial grade) . . .	f 54·08 l 54·69	167·87 161·95	221·95 216·64
4. Do. do.	f 54·01 l 51·85	166·88 168·39	220·89 220·24
5. Ladanum usu Candia . . .	f 113·81 l 114·80	87·88 87·98	201·69 202·78
6. Ladanum in pani (loaves) . . .	f 14·06 l 13·42	47·64 39·46	61·70 52·88

Whereas the French and German grades show a fair degree of concordance, especially in the saponification value

the No. 6 was a very impure specimen, and the values accordingly come out very low. In general, as already stated, the existing commercial grades of labdanum all seem to be more or less artificial products.

Gregor and Bamberger found the methoxyl value = 0. (For the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

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32. Mastic.

Mastix.

Origin and Habitat.—*Pistacia lentiscus* (Anacardiaceæ). Mediterranean littoral; cultivated in Chios.

Chemical Constituents.—Dextro-rotatory ethereal oil ($C_{10}H_{16}$), 2 per cent. (Flückiger). Also various resins, particularly: α -resin ($C_{40}H_{64}O_4$), mastic acid, and β -resin = masticin ($C_{40}H_{64}O$) (Johnston), and bitter principle.

General Properties and Commercial Varieties.—Levantine mastic, the ordinary commercial variety, is in the form of rounded, pale yellow granules (tears) which are hard, with conchoid fracture, and soften when chewed (in which latter respect it differs from sandarach); it is almost entirely soluble in alcohol, ether, chloroform, benzol, carbon di-sulphide, and ethereal oils; but the greater part is insoluble in petroleum ether. *Pistacia terebinthina* yields a balsam resembling mastic, and known as "Chios turpentine" (see Turpentine).

Indian Bombay mastic—little dealt in—comes from Central Asiatic species of *Pistacia* (*P. Cabulica* and *P. Khinjak*). A substitute for mastic is found in "Gommart gum," from *Bursera gummifera*, which should rather be classed with the

elemis (*q.v.*). The name "Gommart" comes from "Gommier" (gum tree) applied to this species of *Bursera*, which is also termed "birch tree" in Jamaica, and belongs to the so-called "incense trees" (see Incense).

"American mastic," formerly so styled, comes from *Schinus molle*, a Mexican *Anacardiacea* (see Hartwich, *die neuen Arzneidrogen*, p. 303).

Adulterants.—Sandarach, colophony (especially in powder), *Resina pini*, sea salt.

Analysis.—Mastic being readily confounded with sandarach, it is advisable, in the first place, to note their points of difference, which will again be dealt with fully under Sandarach. This last named has a higher acid value (S.-Z. ind.), and breaks when chewed, whereas mastic softens. Furthermore, mastic is the more soluble in benzol, and in 60 per cent. chloral hydrate solution (in which sandarach is practically insoluble); both are soluble in 80 per cent. chloral hydrate. In oil of turpentine, mastic is readily and almost completely soluble, whereas sandarach is only partly soluble, and that, too, with difficulty. For the degree of solubility in epi- and dichlorhydrin, see Valenta's table in Part I.

The following values relate to ordinary commercial Levantine varieties (Williams):—

	I.	II.
Acid value, d. (S.-Z. d.) . . .	50.04	56.00
Ester value (E.-Z.) . . .	23.00	23.10
Saponification value, h. (V.-Z. h.)	73.04	79.10
Ash	0.21 %	0.14 %
Moisture	0.97 %	1.46 %

The acid, ester, and saponification values were determined by the usual method. The last-named values, however, should be accepted with caution, since, according to the present state of our knowledge of the chemical com-

position of mastic, the ester-like constituents appear to be absent.

Hirschsohn found—

		Soluble in Petroleum Ether of—		
		b.p. 40° C.	60° C.	80° C.
Mastic	. .	50·96 %	71·56 %	75·86 %
Do.	. .	51·89 %	—	—
Do.	. .	38·49 %	—	—
Bombay mastic	. .	12·50 %	—	12·45 %

Kremel found—

		I.	II.
Acid value, d. (S.-Z. d.)	. .	61·8	70·9

by dissolving the substance in ether alcohol, and redissolving in water as soon as precipitation commenced. The ether and saponification values were not determined.

Von Schmidt and Erban found (by the usual method)—

Acid value, d. (S.-Z. d.)	64·0
Ester value (E.-Z. d.)	29·0
Saponification value, h. (V.-Z. h.)	93·0

Solubility in :—

Alcohol	partial.
Ether	complete.
Methyl alcohol	partial.
Amyl alcohol	complete.
Benzol	„
Petroleum ether	insoluble.
Acetone	partial.
Glacial acetic acid	„
Chloroform	„
Carbon di-sulphide	slight.
Oil of turpentine	partial.

Some kinds appear to be almost entirely insoluble in petroleum ether, whilst others are partially soluble therein.

E. Dieterich found the acid value, d. (S.-Z. d.) = 67·2 by the same method as Kremel.

The author has found that back titration furnishes more concordant results than the direct method, in the case of mastic, and that, moreover, the colour-change from red to yellow is more sharply defined than the converse change in the direct method; the back titration method also dispenses with the necessity for dissolving the substance beforehand. For the reason already given, he did not attempt to determine the ester and saponification values. The method adopted is as follows:—

One grm. of mastic is suffused with 50 c.c. of benzine (sp. gr. 0·700) and 20 c.c. of alcoholic $\frac{n}{2}$ potash, and left for twenty-four hours in a tightly closed glass-stoppered flask, the contents being then titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, without any addition of water.

The values obtained were—

	Acid Value, indirect (S.-Z. ind.)			
	I.	II.	III.	IV.
Mastic electa .	44·80	46·20	44·80	47·60
Mastic electa pulv.	107·80	109·20	110·60	113·40
Mastic naturale .	51·80	53·20	53·20	53·20
Do. .	65·28	65·99	—	—
Mastic, Bombay .	109·20	109·20	103·89	103·89
Do. .	137·60	139·89	—	—
Mastic, Turkish .	90·56	90·26	—	—

The figures agree very well, and show, in the first place, that Indian (Bombay) mastic is distinguishable from ordinary Levantine mastic by its higher acid value, and also that the “pulvis” variety is apparently adulterated (probably with colophony) like nearly all commercial powdered resins (see remarks at end of Part I.). The acid values found by the other authors named also correspond fairly well with the

author's figures. Direct titration furnished somewhat lower values, viz. about 60–65. Preliminary experiments showed that while both aqueous and alcoholic alkali may be used with about the same result, alcoholic alkali alone is more practical and advisable for the detection of any added colophony, the addition of water during titration being also preferably avoided. Tested in the above manner, the Levantine (ordinary commercial) mastics give acid values between 40 and 70, the Bombay kinds 100–140, whilst the Turkish variety is about midway between the two.

Gregor tested the methoxyl value of mastic, and found the same = 0·0–1·9. (For the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

According to Mauch, mastic is partly soluble in both 60 per cent. and 80 per cent. chloral hydrate solutions (see above, distinction from Sandarach). For the Storch-Morawski reaction for detecting colophony, see Colophony.

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33. Resina Pini.

Pine Resin.

Origin and Habitat.—Various species of *Pinus*: *P. Pinaster*, *P. picea*, *P. sylvestris*, *Larix Europæa*. Europe.

Chemical Constituents.—True pine resin contains oil of turpentine, dextro-pimaric acid (m.p. 211° C.), and levo-pimaric acid (m.p. 150° C.), C₂₀H₃₀O₂, which crystallise well.

Tschirch recently succeeded in isolating new “crystallisable resinol acids” (see under Turpentine, and also *Ph. Ztg.*,

1899, No. 77) by fractional separation from pure resins from *Pinus picea*, *P. sylvestris*, and several other species of *Pinus*. In contrast to colophony "Resina Pini" contains esters.

Gallipot is a variety of pine resin, poor in oil, containing pimaric acid, but only a very little ethereal oil.

Barras contains a great deal of impurities, in addition to the above constituents.

The *Resina Pini raffinata* used in pharmacy (*Terebinthina cocta*) is not the same as the above pine resin, but is a residue from the distillation of turpentine, and contains water. It differs from colophony in being—like the hydrated "*Aloe hepatica*"—crystalline and hydrated, instead of anhydrous and amorphous. Anhydrides are found only as traces, if at all, the bulk consisting of hydrates of abietic and allied acids, and ethereal oil is practically non-existent in this variety.

The exudation resin from *Pinus Laricio* has been subjected to a close chemical examination. Bamberger and Landsiedl found—

α -Resin, which is a mixture of abietic pinoresinol ester, with a smaller proportion of paracumaric pinoresinol ester; also pinoresinol, $C_{17}H_{12}O_2(OH)_2(OCH_3)_2$, and β -resin, which is an ester of pinoresinotannol, $C_{30}H_{28}O_4(OCH_3)_2(OH)_3$.

The exudation resin from *Larix decidua* (larch) has also been examined, and found to contain—

Abietic acid and lariciresinol, $C_{14}H_{10}(OCH_3)_2(OH)_3$ (Bamberger and Landsiedl). These authors have more recently determined the formula of lariciresinol to be $C_{17}H_{12}(OCH_3)_2(OH)_4$, two of the four free HO groups being phenolic, the others alcoholic in character. On boiling lariciresinol with acetyl chloride, a tetracetyl derivative, $C_{17}H_{12}(OCH_3)_2(OCH_3CO)_4$, melting at $160^\circ C.$, was obtained; and the action of acetic anhydride on potassium lariciresinol furnished the triacetyl product, $C_{17}H_{12}(OCH_3)_2(OCH_3CO)_3$, m.p. $92^\circ C.$ Two

other derivatives of lariciresinol were also prepared, namely, the di-methyl ether, $C_{17}H_{12}(OCH_3)_4(OH)_2$, and the di-ethyl ether, $C_{17}H_{12}(OCH_3)_2(OC_2H_5)_2(OH)_2$.

General Properties and Commercial Varieties.—

Whereas the resins known as “Resina Pini” are hard, the ordinary turpentine (*q.v.*), also obtained from species of pine, are of soft, balsamic consistence, though more nearly allied to the resins than to the balsams.

Natural pine resin is a sticky, yellowish mass, smelling of turpentine, and mixed with impurities.

Gallipot.—*Resina Pini raffinata* (*Terebinthina cocta*), *Resina alba*, *Pix alba*, and Burgundy pitch are opaque, crystalline masses, with little or no ethereal oil, and of variable colour and water content. Both the last-named properties are dependent on the duration of exposure to heat, and on the melting temperature. *Barras* is only externally impure; otherwise it resembles natural pine resin.

The exudations at the margin between the blaze and the bark in black fir are covered with a peculiar resin to which the term exudation resin has been applied (see above), and which, though merely of theoretical interest, is worthy of mention.

Adulterants.—Vegetable and mineral impurities, artificial products from colophony, oil of turpentine, and oil of worm-wood.

Analysis.—In view of the divergent names applied to pine resins, especially gallipot, *Resina Pini*, *Resina Pini raffinata* and *depurata*, and also of the fact that, in many countries, *Resina Pini raffinata* and different intermediate kinds of pine resin are called gallipot, it cannot be surprising that the analytical data show only a relative degree of concordance. In addition comes the circumstance that the

percentage of ethereal oil plays a great part in influencing values, just as with the gum resins. Whereas colophony contains no esters, these bodies are present in all varieties of *Resina Pini*, and hence the existing ester and saponification values must be regarded as justified.

A. Kremel found—

	Acid Value, d. (S.-Z. d.).
I. Resina Pini	77·8
II. Resina Pini depurata . .	102·6
III. Pix burgundica	142·2

by the direct method, but did not examine the ester and saponification values.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	145·44–161·16
Ester value (E.-Z.)	9·95– 28·66
Saponification value, h. (V.-Z. h.).	157·16–188·96
Loss at 100° C.	12·50 per cent.
Ash	1·0 „

Solubility in—

Alcohol (90 per cent.)	complete.
Chloroform	„
Acetic ether	„
Benzol	„
Carbon di-sulphide	„
Ether	almost complete.
Oil of turpentine	94·28 % soluble.
Petroleum ether	84·95–97·60 % sol.

The author found—

Acid value, d. (S.-Z. d.)	151·18–159·13
Ester value (E.-Z.)	12·03– 27·31
Saponification value, h. (V.-Z. h.).	163·23–179·94

And later—

Acid value, d. (S.-Z. d.)	149·80–155·35
Ester value (E.-Z.)	12·64– 29·40
Saponification value, h. (V.-Z. h.)	165·11–179·67

Together with the following acetyl values :—

Acetyl	{ Acid value (A.-S.-Z.)	155·27–158·48
	{ Ester value (A.-E.-Z.)	64·38– 75·48
	{ Saponification value (A.-V.-Z.)	222·86–230·75

(For the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

With the exception of Kremel's figures the values agree very well, and show that this means is of no more use for differentiating the various kinds of *Resina Pini* than it is for the turpentine (*q.v.*).

According to Maisch, artificial products, made of white pitch, oil of turpentine, and oil of wormwood, are met with in commerce. For the detection of pine resin and colophony in other resins by the Storch-Morawski reaction, see Colophony.

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34. Sandarach.

Resina Sandaraca.

Origin and Habitat.—*Callitris quadrivalvis* (Coniferæ). North-West Africa. (For the Australian sandarachs, see end of section.)

Chemical Constituents.—Sandaracolic acid ($C_{44}H_{65}O_5$ -COOH), 85 per cent.; callitrolic acid ($C_{64}H_{82}O_5$ (OH) COOH), 10 per cent.; ethereal oil and bitter principle, 2·84 per cent.; water, 0·56 per cent.; ash, 0·1 per cent.; impurities, 1·5 per cent. (Balzer).

Tschirch has recently succeeded in isolating new "crystalisable resinol acids" from sandarach by fractional separation with $(NH_4)_2CO_3$ and Na_2CO_3 . (Compare Dammar, and see also *Ph. Ztg.*, 1899, No. 77.)

General Properties and Commercial Varieties.—

Ordinary African (Morocco) Mogador sandarach is in the form of somewhat elongated, yellowish lumps, which are dusty on the outside, and break down into powder when chewed, instead of softening—thus differing from mastic. It is completely soluble in alcohol and ether, but only partially so in carbon di-sulphide, chloroform, oil of turpentine, and petroleum ether, and less so in benzol. Australian and Tasmanian sandarach (from other kinds of *Callitris*) and West Indian sandarach (which is of doubtful origin) are practically out of the market. This remark also applies to the so-called “German” sandarach, a granular resin occasionally found under the bark of the juniper. A few varieties of sandarach—*e.g.* Australian—are found as “soft copal” in commerce.

Adulterants.—Mastic, colophony (especially in powder), Resina Pini, and dammar.

Analysis.—African sandarach being the principal commercial variety, whereas Australian sandarach is only met with in isolated parcels, the analytical data of the former kind may well be given first.

It may be premised that—as in the case of copal—the different age of the samples must be blamed for the divergent and often very contradictory results obtained. This applies to the percentage of solubility in alcohol, ether, benzol, or petroleum ether, as well as to the acid value and sp. gr.

Williams found—

	I.	II.
Acid value, d. (S.-Z. d.)	154.0	145.6
Ash	1.88 per cent.	1.44 per cent.
Moisture	0.04 „	0.17 „

The ester value was so low that Williams gave prominence to the large amount of free acid over the small quantity of

esters. The acid value was determined by the usual method of direct titration.

Von Schmidt and Erban found—

Acid value d. (S.-Z. d.) . . . 140.0 (“usual” method).

Solubility in—

Alcohol	soluble.
Ether	”
Methyl alcohol	partially soluble.
Amyl alcohol	soluble.
Benzol	almost insoluble. ¹
Petroleum ether	insoluble.
Acetone	soluble.
Glacial acetic acid	partially soluble.
Chloroform	” ”
Carbon di-sulphide	almost insoluble.
Oil of turpentine	partially soluble.

Flückiger found solubility in—

Pure absolute alcohol	} completely soluble.
Ether	
Amyl alcohol	
Acetone	
Chloroform	partially soluble.
Ethereal oils	” ”
Benzol	insoluble. ²

Hager found—

Sp. gr. 1.078–1.088

Kremel found (direct method)—

Acid value, d. (S.-Z. d.) . . . 144.20

¹ See note on Flückiger's observations.

² As found by von Schmidt and Erban, sandarach is only “almost insoluble” in benzol, the author having found up to 40 per cent. soluble. (See “Adulterated Sandarach” further on.) A specimen entirely insoluble in benzol is, according to existing experience, a rarity.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	97·53–123·20
Soluble in chloroform	23·15 per cent.

The ester and saponification values given by this author are omitted, sandarach being free from esters.

Hirschsohn found—

Soluble in petroleum ether	7·0–8·0 per cent.
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The author finds that the only way to ensure complete combination of the resin acids, in titrating sandarach, is by indirect titration. In this method it is unnecessary to dissolve the resin beforehand, the alkali acting as a solvent, as well as combining quantitatively with the resin acids; moreover, the colour-change from red to yellow is much more accurately noticeable than is the case in direct titration.

The author works as follows:—

(a) *Acid value, ind.* (S.-Z. ind.).—One grm. of sandarach is suffused with 20 c.c. of alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0·700), and left to stand for twenty-four hours in a tightly closed vessel, at the end of which time the contents are titrated back with $\frac{n}{2}$ sulphuric acid, without any addition of water. The volume (c.c.) of KHO combined, multiplied by 28·08, gives the acid value.

(b) *Ash determination.*—Two grms. of sandarach are carefully incinerated, and calcined until found of constant weight after cooling in a desiccator.

Preliminary experiments showed that alcoholic alkali used alone is far preferable to mixed alcoholic and aqueous potash, being simpler in practice even though there is but little difference in the resulting values. Moreover, direct titration gave lower and less concordant values, and a less precise

colour-change at the end-point. Finally, the indirect titration method obviates the necessity for preparing a solution of the resin beforehand.

The following values (in round numbers) were furnished by numerous specimens of African sandarach:—

Mogador (Morocco) sandarach—

Acid value, ind. (S.-Z. ind.)	130-160
Acid value, d. (S. Z. d.)	90-110
Ash	<i>nil</i>

and the author would lay down the condition that a pure sandarach should be practically free from ash, in addition to giving the above acid values, direct and indirect. For the solubility of sandarach in epi- and di-chlorhydrin (Valenta), see table in Part I.

With regard to the differentiation of sandarach from mastic, the higher acid value (ind.) of the former affords a means to this end; moreover, sandarach pulverises when chewed, whereas mastic softens, and, again, the latter is the more soluble in benzol. Furthermore, according to Mauch, sandarach is practically insoluble in 60 per cent. chloral hydrate, in which mastic is partially soluble, both being soluble in the 80 per cent. solution of this reagent. Mastic is more readily soluble in oil of turpentine than sandarach. Adulteration with colophony or Resina Pini forces the acid value (ind.) upwards, and considerably increases the percentage soluble in petroleum ether, whilst dammar, with its low acid value, depresses this constant. For the detection of colophony by the Storch-Morawski reaction, see Colophony.

The author has reported as follows, on the examination of an adulterated sandarach:—

“The adulterated specimen could not be distinguished in the slightest degree from pure sandarach by its outward appearance, so that buyers who—as is unfortunately the

general custom—purchase by the appearance alone, would not notice anything in the least degree remarkable about it. Also, the qualitative solubility in alcohol, ether, benzol, and petroleum ether did not, at first sight, appear abnormal. The quantitative examination, however, turned out altogether differently; the adulterated specimen examined in this laboratory, by H. Mix, furnishing the subjoined interesting values:—

1. Soluble in 60 per cent. chloral hydrate solution .	6·80 per cent.
2. Insoluble in 60 per cent. chloral hydrate solution .	93·20 „
3. Insoluble in petroleum ether	6·89 „
4. Soluble in petroleum ether	93·11 „
5. Insoluble in benzol	2·74 „
6. Soluble in benzol	97·26 „
7. Acid value, ind. (Dieterich method)	$\left\{ \begin{array}{l} 173·98 \\ 175·50 \end{array} \right.$

“On the other hand, pure sandarach, according to Mauch, is practically insoluble in the above chloral hydrate solution (we found up to 4 per cent. soluble). In benzol, sandarach is almost insoluble, according to von Schmidt and Erban, or quite insoluble, according to Flückiger; but the author cannot confirm the great pharmacologist's results in this respect, having, like von Schmidt and Erban, found partial solubility—in fact up to more than 40 per cent. (see below).

“According to Hirschsohn, the solubility of pure sandarach in petroleum ether does not exceed 8 per cent. The author's researches, so far, show the normal acid value to be about 140, and the direct acid value in both pure and adulterated specimens is lower than by the indirect method. As colophony considerably raises the acid value, and is also much more soluble than sandarach in chloral hydrate, benzol, and petroleum ether, the above values given for adulterated sandarach clearly show that the specimen was an artificial product of sandarach and colophony. The adulterated

sample was also more readily soluble in alcohol than the pure drug. Haberlé succeeded in isolating from the falsified product the characteristic resin acids of colophony.

"It should be mentioned that, speaking generally, the adulteration had been so cleverly manipulated that only the above accurate quantitative testing was able to reveal the true nature of the product.

"The discoveries of Haberlé, the appearance of the specimen, which agreed exactly with that of Mogador sandarach, and the circumstance that the goods were designated real sandarach, precluded the possibility of their being some other kind of sandarach of unknown origin. Australian sandarach was also excluded from possibility by the fact that its acid value—as the author was able to quickly show—is never so high as that of true sandarach."

The more recent methods of examination have also been applied to sandarach, the author having, for example, determined the acetyl values—

Acetyl	{ Acid value (A.-S.-Z.)	166.03–169.83
	{ Ester value (A.-E.-Z.)	73.59– 81.60
	{ Saponification value (A.-V.-Z.)	239.62–251.43

Kitt found the following carbonyl values:—

$$\text{C.-Z.} = 0.43\text{--}0.74$$

Gregor and Bamberger found the methoxyl value = 0, notwithstanding that Tschirch and Balzer have shown the presence of a methoxyl group in sandaracolic acid.

(For the worth of these last-named determinations, see *Chem. Rev.*, 1898, No. 10.)

In conclusion, the results obtained up to the present with Australian varieties of sandarach may be given (compare Maiden's valuable treatises cited in the Bibliography at foot). This authority gives the following particulars with regard to the origin, properties, etc., of Australian sandarachs:—

Callitris cupressiformis, Vent.—This is found all over Australia, except in West Australia, and is one of the best known species. The resin is water-white, transparent, and clear; on prolonged storage it assumes a slight coloration, without, however, losing any of its lustre.

C. calcarata, R. Br.—Found from North Victoria to Central Queensland. The resin is pale yellow, and thickly coated with flowery dust. Is insoluble in water, but soluble to a small whitish residue in alcohol. Petroleum ether dissolves out 5 per cent. of a perfectly colourless transparent resin. A second very fine specimen, pale yellow in colour, and with an excellent aroma, was soluble in alcohol, except for 1·3 per cent. of residue, and furnished a pale yellow and perfectly clear solution. Petroleum ether took up 22·1 per cent. A third sample proved of quite different character. It had the consistence and general constitution of Manila elemi, but differed from this substance by its flesh-tint colour and purely turpentine smell. The sample was the more remarkable from the fact that the same tree also yielded sandarach of the ordinary colour.

C. columellaris, F. v. M.—New South Wales and Queensland. The resin is rather pale; alcohol dissolves 95·4 per cent. to a pale yellow solution; petroleum ether, 35·8 per cent. to a clear, colourless liquid. This high solubility, as compared with all other kinds of sandarach, in petroleum ether is specially noteworthy.

C. verrucosa, R. Br.—Botanical Garden, Sydney. Very dark resin, soluble to the extent of 97·5 per cent. in alcohol, and 22·8 per cent. in petroleum ether. The same variety was formerly reported on by Morel, and consisted of pale yellow tears, thicker and longer than ordinary sandarach, covered with white dust, and of agreeably aromatic odour, with bitter aromatic taste.

Supplementing the labours of Maiden, Clarke stated that Mogador (*i.e.* African) sandarach is better and purer than Australian. This may be the reason why the latter has not made its way.

In addition to the foregoing general properties and solubilities, the following analytical data on Australian sandarach have been published by the author. The acid values alone were determined, the indirect method, already described, being employed:—

		I.	II.
		Acid Value, ind.	
		(S.-Z. ind.).	
Australian sandarach	139·00	139·00
Do.	fine selected	129·87	130·57
Do.	seconds	144·61	144·61
Do.	ordinary	155·84	157·28

According to these figures, the acid values of the best Australian sandarachs are not so high as those of the African product; nevertheless, great similarity exists between the two kinds.

For Asia Minor sandarach the author found—

Acid value, ind. (S.-Z. ind.) 179·01–179·71

The pure resin acids from African sandarach gave the acid values, ind., 141·10 and 141·10, which agree with the average furnished by natural sandarach.

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35. Scammonium.

*Resina Scammonium.*¹

Origin and Habitat.—*Convolvulus Scammonia*, L. (Convolvulaceæ). Aleppo, Smyrna.

Chemical Constituents.—Since both the Aleppo and Smyrna varieties are very impure, the product (Resina scammonium) artificially prepared from the roots is generally vended and used.

The chief constituent is Scammonin $C_{34}H_{56}O_{16}$, which, according to Spirgatis, is identical with Jalapin = Orizabin.

General Properties and Commercial Varieties.—Aleppo scammonium, or “usu Aleppo,” is in the form of light, opaque, rough lumps, with edges more or less sharp, and of a greenish ashy grey colour. The fracture shows a faint waxy lustre, not greasy; the flavour is very disagreeably irritant; the resin forms an emulsion with water.

Scammonium “in tears,” a very pure variety, is no longer in the market.

Smyrna scammonium forms dense, heavy lumps and cakes, of a dark, almost black, colour, and wax-lustrous fracture; the resin does not emulsify in water. Aleppo scammonium if pure (see below) is more valuable than the Smyrna variety.

French scammonium, from *Cynanchum acutum*, is no longer met with in commerce.

All varieties of scammonium, particularly that from Aleppo, being very impure, the natural resin is generally replaced, for pharmaceutical purposes, by “Resina scammonium,” prepared from the root of *Convolvulus Scammonia*. It takes the form of lumps or sticks, dull on the outside

¹ More precisely speaking, the Aleppo Scammonium should be called “juice,” and that recovered from the root, “resin.”

but lustrous on the surfaces of fracture; is soluble in alcohol, and has an aromatic odour.

With regard to the resin from *Convolvulus althæoides*, see Resina Jalapa.

Adulterants.—Artificial products, from chalk, resin, colouring matters, and extractives, containing up to 50 per cent. of mineral substances.

Analysis.—Aleppo scammonium is a resin that has always been subjected to more adulteration than probably any other known kind; for which reason it has had to be replaced in pharmacy by the resin obtained from the roots aforesaid. The following communication made by Thompson may be cited to show the almost unexampled adulteration practised on scammonium. An alleged scammonium received by this authority exhibited little claim to be considered pure, even under external examination. Nevertheless it was labelled, "Scammonium containing 84 per cent. of scammonin," the formula $C_{32}H_{56}O_{16}$ being appended. The specimen, which is said to have come from a German firm of drug merchants, consisted of irregular, greenish black, hard, horny lumps, with a resinous fracture, and difficult to pulverise, and contained—

Soluble in ether	0·4 per cent.
Soluble in alcohol	2·0 „
Soluble in water	42·6 „
Starch, and a little cellular matter .	43·0 „
Moisture	12·0 „

On combustion there remained 2·12 per cent. of ash (43·6 per cent. of which was soluble in water) containing K, Mg, Ca, Fe, and Si in the form of carbonates and sulphates, together with a trace of chlorides. The portion soluble in water was nothing but gum arabic, the insoluble consisting of starch and a little cellular substance.

H. Greenish also reports on the multifarious adulterations of Aleppo scammonium with starch, wood ashes, soil, gum, tragacanth, powdered roots, etc. Rebner examined five commercial varieties of "Resina," and found one of them to be entirely soluble in ether, the solubility of the others being 26, 40, 78, and 79 per cent. respectively. Three of them contained starch.

Hess examined the following kinds of scammonium:—

I.	Resina scammonium	.	.	.	fusc. Ph. G.
II.	Do.	.	.	.	alb.
III.	Do.	.	.	.	Ph. G.
IV.	Do.	.	.	.	Ph. Holl.
V.	Do.	.	.	.	Ph. Suecic.

and found—

I.	had the sp. gr.	1·142	and	2·2%	of moisture.
II.	„	1·107–1·112	„	4·5%	„
III.	„	1·104–1·110	„	4·0%	„
IV.	„	1·120	„	5·4%	„
V.	„	1·160	„	4·3%	„

He recommended the root resin purified with bone black, and rightly required that this resin should be perfectly soluble in cold alcohol. According to Möller, Aleppo scammonium should not contain over 8 per cent. of ash—a condition fulfilled by few of the highly adulterated samples now current. The concensus of experience is in favour of the introduction of the resin prepared from roots, to replace the very bad and impure Aleppo scammonium.

The root extract is prepared by exhausting the powdered root with strong alcohol, the product being purified with charcoal if required. According to E. Dieterich, the yield obtained is about 10 per cent. Dönsch published a report on the *Resina scammonium* extracted from root, and found that the root yielded a little over 5 per cent. of (repeatedly

purified) resin. On the other hand, three commercial samples behaved differently, and furnished an ash which was not perfectly soluble in dilute hydrochloric acid. The acid solutions contained lime in some cases, magnesia in others. The low degree of purity of the commercial products is probably the cause of the difference in the behaviour of the ash, etc., in comparison with the pure scammonium prepared in the laboratory. In any case, the commercial "Resina" prepared from root is of much greater purity than Aleppo scammonium.

Isolated instances of acid value (direct), ester value, and saponification value determinations are to be found in the literature of the subject.

Kremel found (by the usual method)—

	Aleppo Scammonium.	"Resina." Scammonium.
Acid value, d. (S.-Z. d.)	8.2	14.6
Ester value (E.-Z.)	172.0	171.0
Sapon. value, h. (V.-Z. h.)	180.2	185.6

From these figures it would seem that Kremel had a very pure specimen of Aleppo scammonium, since the values are almost the same as those from the extracted resin.

E. Dieterich determined only the iodine value; Gregor and Bamberger the mexthoxyl value, which they found = 0. (On the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

The alcoholic root extract (commercial "Resina scammonium") should, in the first place, be soluble in alcohol without leaving any appreciable residue, and should not contain any notable proportion of ash. Aleppo scammonium is often used, instead of root, for preparing "Resina," by a method of purification with alcohol and charcoal. From the point of view of the purity of the final product, this

method cannot be recommended, the alcohol extracting the foreign resins (colophony, etc.) pre-existing in the Aleppo scammonium, which are therefore conveyed into the purified product,—an occurrence that is, of course, impossible in the case of the root. In view of the drastic action of scammonium, a maximum degree of purity is necessary in the “Resina,” and the requirements should be made correspondingly stringent. Hooper believes that the variable percentage of resin in the roots is attributable to the condition of the soil, especially with regard to the percentage of phosphates.

For the detection of colophony in scammonium by the Storch-Morawski reaction, see under Colophony.

An instance of gross adulteration of scammonium is reported in the *Ap. Ztg.*, 1899, No. 47.

A sample tested on account of its suspicious appearance—it exhibited peculiar small cavities, interspersed with tiny grey and blackish blue metallic-looking crystalline spangles—was found, on extraction with ether, to contain 41·3 per cent. of resins, whereas good commercial specimens should exhibit 75–80 per cent. The ash content was 16·6 per cent., against 3–8 per cent. (highest) in good scammonium. The residue, insoluble in ether, contained a large proportion of starch; and a considerable amount of lead sulphide was also detected. (*Petit Moniteur de la Pharmacie*, 1899, p. 3208.)

This dangerous adulteration recalls the equally dangerous artificial coloration of shellac with arsenic sulphide (*see* Shellac).

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36. Shellac.

Resina Lacca.

Origin and Habitat.—Product of the lac insect, *Coccus Lacca* Keor, on—*Croton lacciferum*, or Bihar tree (Euphorbiaceæ); *Ficus religiosa*, or Pepel tree (Artocarpeæ); *Butea frondosa*¹ and varieties of *Butea* (Papilionaceæ); and on *Chenopodium anthelminticum* (stinking weed). Ceylon, Antilles, Farther India.

Chemical Constituents.—Wax, 6 per cent.; laccin pigment, 6·5 per cent., with laccinic acid ($C_{16}H_{12}O_8$); pure resin, 74·5 per cent., of which 35 per cent. is soluble in ether and contains scent, a portion of the resinous substance, and erythrolaccin. The remaining 65 per cent. of the pure resin is insoluble in ether, and contains the resinotannol ester of aleuritic acid. (The formula of this acid is $C_{13}H_{26}O_4$.) The instability of the resinotannol has hitherto rendered a close investigation impossible. The impurities comprise sand, fragments of wood, etc., 9·5 per cent.; water, 3·5 per cent. (Farner).

General Properties and Commercial Varieties.—The stick lac is deprived of its pigmentary matter, which then comes into commerce as “lac dye.” The resinous residue is vended as *Lacca in tabulis* (plates) or *Lacca in granis* (granular), according to the colour. The perfectly white bleached lac is met with in commerce as *Lacca alba*, in the form of twisted sticks, and is the purest, most valuable, and most free from colouring matter. The colour of the foregoing grades varies between white and dark reddish brown. As is well known, shellac is largely used in varnish-making.

¹ This gum lac, from *Butea*, should not be confounded with Bengal kino (*q.v.*); also from *Butea frondosa*, which resin is obtained from the tree trunk.

The so-called "Arizona shellac" or "Sonora gum" comes from *Larrea Mexicana* (Zygophyllæ). On the other hand, according to Hartwich, *Mimosa laccifera* furnishes a "Sonora gum," produced as a granular lac by the insect *Carteria Mexicana*.

Adulterants.—Colophony, aloe resin, arsenic sulphide, orpiment (?).

Analysis.—Colophony, and other cheap resins (as also aloe resin), being used to adulterate shellac, particular attention has been devoted to the solubility of shellac in alcohol, petroleum ether, and ether.

Hirschsohn tested the solubility of numerous specimens in petroleum spirit, cold and hot, and obtained the following results :—

				Per cent. soluble—	
				Dried at 17° C.	at 120° C.
1.	Lacca	in baculis	. .	14.01	5.52
2.	Do.	do.	. .	13.23	6.31
3.	Do.	do.	. .	14.25	4.84
4.	Do.	in massis	. .	3.37	1.27
5.	Do.	do.	. .	3.60	2.07
6.	Do.	do.	. .	2.80	1.90
7.	Do.	do.	. .	3.00	1.86
8.	Do.	in tabulis	. .	1.22	0.40
9.	Do.	do.	. .	1.30	0.70
10.	Do.	do.	. .	1.80	1.30
11.	Do.	do.	. .	1.20	0.80

Oberdörffer first drew attention to the adulteration of shellac with colophony, and recommended the sp. gr. and solubility in ether as a test for this admixture (pure shellac with 25 per cent. of colophony gives the sp. gr. 1.120). The natural wax, of which shellac contains up to about 5 per cent., passes into the ether, a larger percentage of soluble matter indicating colophony. In this connection it should be observed that the percentage of wax fluctuates

considerably. Oberdörffer found 5 per cent., Farner 6 per cent.; Benedikt and Ulzer found only 0·5 to 1 per cent. for the wax recovered by means of sodium carbonate; finally, Gascard also obtained 6 per cent. of resin. The specimens examined by the last named and Farner would, according to Oberdörffer's views, be regarded as adulterated with colophony!

Other adulterants are aloe resin, and, according to Mackey, artificial coloration with orpiment, yellow arsenic sulphide, is also practised. These last-named substances remain behind when the substance is treated with alcohol. Colophony should also be detected by the aid of petroleum ether, which dissolves only three per cent. of pure shellac, whereas colophony is in some cases entirely soluble, in others only to the extent of about one-half. According to the foregoing data by Hirschsohn, the limit of 3 per cent. does not appear to be tenable, since he found 14 per cent. of substances (dried at 17° C.) soluble in petroleum ether.

In any event, these reports are all so uncertain that we can only agree with the following opinion expressed by Klar—so far as concerns the solubility of shellac:—

Klar says: "In the literature of the subject it is generally prescribed that bleached shellac should not exhibit more than 5 per cent. soluble in ether (colophony test). The author has also determined the acid and ester values, and found that the wax content exercises a considerable influence on the ethereal extraction value, which, however, as well as the acid and ester value, is apparently of little importance, the values furnished by commercial specimens being so divergent. At present there is no certain, and at the same time simple, method for detecting adulteration in bleached shellac. Its solubility in 96 per cent. alcohol

may be influenced partly by the presence of wax, partly by overbleaching, and partly by alterations due to the action of atmospheric air, since, unless stored under water, shellac gradually loses its solubility in alcohol under the influence of the air. None of the attempted filtration or clarification experiments have been successful. Should the bleached shellac—and a small addition of wax would do no harm for polishing purposes—not give a clear solution, Klar recommends a slight addition of zinc oxide, which forms a compact substance with the waxy matters if the mixture be left to stand in the warm, whereby one is enabled in a short time to pour off a clear liquid, though a by no means minute percentage of shellac is also thrown down.”

As regards the acid, ester, and saponification values mentioned by Klar, various figures are met with for these in the literature of the subject.

Williams found (usual method)—

Shellac.	Ash %	Moisture %	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).
Medium button .	1.06	0.28	63.00	140.03	203.03
Garnet .	0.72	0.37	56.00	156.60	212.60
Fine orange .	1.23	0.31	64.00	142.00	206.00
Good 2nd orange .	0.88	0.42	47.60	163.10	210.70
Fair do.	1.01	0.63	56.00	155.40	211.40
Inferior do.	1.41	0.94	57.40	136.70	194.10

Kremel found by the same method—

Shellac.	Acid Val., d. (S.-Z. d.).	Ester Val. (E. Z.).	Sap. Val., h. (V.-Z. h.).
White	73.7	102.8	176.5
Yellow	63.5	50.2	113.7
Lacca in granis (Alc. dep.) .	—	—	174.8

Von Schmidt and Erban found—

Shellac.	S.-Z. d.	E.-Z.	V.-Z. h.
Brown . .	65.1	148.2	213.3
Orange . .	60.0	151.6	211.6

Solubility in—

Alcohol	soluble.
Ether	insoluble.
Methyl alcohol	soluble.
Amyl alcohol	"
Benzol	almost insoluble.
Petroleum ether	insoluble.
Acetone	almost insoluble.
Glacial acetic acid	soluble.
Chloroform	partly soluble.
Carbon di-sulphide	insoluble.
Oil of turpentine	almost insoluble.

The solubility in ether and petroleum ether should, according to other authorities, be more correctly classed as "slightly soluble." According to Mauch, both "*Lacca in tabulis*" and "*Lacca depurata in bacillis*" are soluble in 80 per cent. chloral hydrate, in which they first swell up.

The above acid, ester, and saponification values fluctuate within comparatively narrow limits; and one may hope—against the opinion of Klar—that these characteristics may afford a means of detecting adulteration. A thorough investigation of this matter would be a task as thankworthy as it is desirable.

On the solubility of bleached shellac in epi- and di-chlorhydrin (Valenta), see table in Part I.

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37. Storax.

Balsamum Styracis (officinal in Germ. Pharm. III.).

Origin and Habitat. — *Liquidamber orientalis*, M. (Hamamelideæ). Asia Minor.

Chemical Constituents.—Styrol ($C_6H_5.CH=CH_2$), Cinnamic acid ($C_6H_5.C.H.CH.COOH$), Styracin = Cinnamic cinnameter ($C_9H_7O_2.C_9H_9$), Cinnamic phenylpropyl ester ($C_6H_5.CH=CHCOOCH_2CHC_6H_5$), Cinnamic ethyl ester ($C_9H_7O_2.C_2H_5$), vanillin (K. Dieterich), ethyl vanillin (von Miller), α - and β -storesin ($C_{35}H_{55}(OH)_3$), amorphous resin, traces of benzoic acid, and cinnamic storesin ester (von Miller).

American storax from *Liquidamber styraciflua* contains styrol, styracin, oxygenous oil, cinnamic phenylpropyl ester, and storesin (von Miller).

General Properties and Commercial Varieties. — Ordinary storax, from Asia Minor, is a turbid, hydrated, viscid, sticky, grey balsam, of spicy, irritant flavour, and with an odour like benzoin. It is partly soluble in benzol and petroleum ether, and almost completely so in ether and alcohol. Under the microscope it exhibits crystals. Formerly the name Storax was also applied to the resin from *Styrax officinalis*, for which reason this tree is still often—though erroneously—classed as a storax producer (see below, under *S. calamitus*). “Purified storax” (by treatment with ether) is turbid, thickish, sometimes crystalline, light brown; that purified with benzol, benzine, or alcohol is of a faint dark brown colour and thick consistence. A so-called strained (“koliert”) storax is a crude product, freed from the coarser impurities and water, and is intermediate between the quite crude and the purified article.

A Styrax cum oleo olivarum is used as another solution

or emulsion in pharmacy for convenience in dispensing, and is favoured by the medical profession as being easy to triturate and manipulate for use in cases of itch, etc.

American storax is known in America as "sweet gum," and comes from *Liquidamber styraciflua*; it is mostly used for chewing. According to Guibourt, this balsam is identical with (white) Peruvian balsam (*q.v.*). A storax balsam which, however, is used solely in the country as a remedy for Psoriasis, is derived from *Microstemon* (Anacardiaceæ). The residual expressed bark left from the preparation of storax is used as a fumigant, under the name *Styrax calamitus*; and a mixture of storax and sawdust is also sold under the same title, as was also formerly the case with the resin from *S. officinalis* for the same purpose.

The origin, derivation, and pharmacognosis of the varieties of storax have been described by Möller (*Ap. Ztg.*, 1894, p. 752; 1896, p. 207; 1897, p. 596).

Adulterants.—Turpentine, colophony, castor oil, olive oil, and fatty oils in general, vegetable impurities, and water. At one time labdanum also was used to adulterate storax.

Analysis.—A good many investigations have been undertaken on storax, particularly with regard to its purification and the preparation of a uniform product suitable for medico-pharmaceutical purposes. The irregularity and adulteration of storax have also been referred to on various sides; occasionally it would seem that artificial products alone are found in commerce. Recently the author examined authentically pure specimens of storax taken direct from the parent tree, and laid the first foundations of the scientific testing and valuation of this product. As in the case of Peruvian balsam, these researches showed that the commercial varieties—a large number of which were examined—were quite different in composition to the pure natural drug. This

—which was also referred to by earlier authorities, such as Mylius, Gehe & Co., and others—seems still to be the case, and, apparently, perfectly pure commercial storax is practically non-existent.

The various kinds and forms of storax will now be dealt with in detail *seriatim*.

I. Crude Storax (*Styrax liquidus crudus*). — The numerous examinations made for acid, ester, saponification, and iodine values, and the results obtained, are of merely relative worth in the valuation of storax, because for the most part the determinations were made with alcoholic extracts, and not with the natural storax. The disadvantages of using only portions of a drug, instead of the crude product, have already been fully dealt with in these pages, and therefore need only be mentioned here. It is not clear from the reports of Kremel, Beckurts and Brüche what methods these authors employed, and we must therefore leave it an open question whether they worked with an extract, the crude product, or some other form. At all events, E. Dieterich, Evers, and others used extracts. The present author has recently worked out a method which is suitable for direct application to crude storax, and therefore enables reliable conclusions to be formed with regard to the natural drug.

Just as attention was directed by Gehe & Co., Mylius, and others to the existence of adulteration, so various proposals have been made for detecting the same. Thus, E. Dieterich proposed to employ the acid value (direct) for this purpose, seeing that turpentine (ordinary, not Venice, turpentine) and colophony give higher acid values than storax. Similarly, Beckurts and Brüche advocated the ether, saponification, and iodine values for detecting adulteration; and Evers believed that the iodine value, and sp. gr. in particular, were worthy of recommendation.

Hirschsohn examined several samples for the amounts (dried at 17° and 120° C.) taken up by petroleum ether, and found—

	Per cent. soluble—	
	Dried at 17° C.	at 120° C.
(1)	59·12	52·09
(2)	43·30	32·82
(3)	54·76	47·98

After being heated to 120° C. the residues were colourless, almost inodorous, oily, sometimes setting to a crystalline mass.

According to Hager, the adulteration of storax with turpentine can be detected by petroleum ether.

A. Kremel found—

Acid value, . (S.d-Z. d.)	47·6
Ester value (E.-Z.)	31·9
Saponification value, h. (V.-Z. h.)	79·5

by the usual method.

Von Schmidt and Erban found—

Acid value, d. (S.-Z. d.)	179·5
Ester value (E.-Z.)	68·8
Saponification value, h. (V.-Z. h.)	198·3

by the same method as Kremel.

Solubility in.—

Alcohol . . .	partly soluble.	Petroleum ether .	insoluble.
Ether . . .	„	Acetone . . .	partly sol.
Methyl alcohol	„	Glacial acetic acid	„
Amyl . . .	„	Chloroform . .	„
Benzol . . .	„	Car. di-sulphide .	slightly sol.
Oil of turpentine . . .	partly soluble.		

E. Dieterich found—

With extract	Acid value, d. (S.-Z. d.)	37·19– 96·65
	Ester value (E.-Z.)	74·60–168·00
	Saponification value, h. (V.-Z. h.)	134·60–249·00
	Ash . . .	0·07– 1·20 per cent.
	Loss at 100° C. . .	10·25– 40·15 „

Solubility in—

Alcohol (90 per cent.)	. . .	56·14–84·00 per cent.
Acetic ether	. . .	69·40–73·60 „
Chloroform	. . .	69·20–72·60 „
Ether	. . .	65·80–82·80 „
Benzol	. . .	64·80–74·80 „
Oil of turpentine	. . .	54·40–57·80 „
Carbon di-sulphide	. . .	62·30–67·80 „
Petroleum ether	. . .	15·00–19·40 „

The acid, ester, and saponification values were determined from an alcoholic solution of the alcoholic extract by the same method as employed by Kremel.

Beckurts and Brüche found—

No.	Sp. gr.	Solubility in own vol. of Alcohol.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sap. Val., h. (V.-Z. h.).
1.	1·116	61 per cent.	80	113	193
2.	1·121	72 „	91	120	214
3.	1·113	62 „	68	112	180
4.	1·113	66 „	69	153	222
5.	1·120	71 „	75	130	205
6.	1·118	64 „	93	115	208

The acid, ester, and saponification values were found by the usual method, but it is not clear whether the unfiltered solution (*i.e.* the crude product) or the alcoholic solution of an extract was used.

The author has obtained the following figures, the constants being furnished by the extract:—

		I.	II.
Loss at 110° C.		19·43 per cent.	24·05 per cent.
Ash		0·35 „	0·71 „
Soluble in alcohol		77·43 „	73·87 „
Insoluble		4·23 „	3·36 „
From the extract	Acid value, d. (S.-Z. d.)	57·51	57·90
	Ester value (E.-Z.)	—	—
	Saponification value, h.	—	—
	(V.-Z. h.)	—	—

Evers says—

“The directions of the (German) Pharmacopœia are altogether insufficient, and a storax adulterated with 10–20 per cent. of turpentine will pass the Pharmacopœia test completely. The estimation of the sp. gr.—especially at 100° C., in a manner similar to that of E. König for testing butter fat—is of the greatest value for detecting adulteration; all extraneous admixtures, such as turpentine, colophony, fats, and oils, reducing the sp. gr. The test should be performed with purified storax, which has been heated in a water oven (at 100° C.) for about three hours, in order to drive off any remaining alcohol.¹ The sp. gr. reading is not taken until the storax has attained the temperature of 100° throughout the entire mass. To facilitate this, it is advisable to carefully raise and lower the spindle—which is set at 100° C., and provided with a scale for sp. grs. between 1·095 and 1·120—several times in the storax. The sp. gr. of purified storax is 1·109–1·114; that of the crude product, merely deprived of water and clarified by subsidence in the warm, being somewhat higher. An addition of 10 per cent. of turpentine reduces the sp. gr. considerably. Purified storax, showing a sp. gr. of less than 1·107 at 100° C., should be regarded with suspicion at least; and if the sp. gr. be lower than 1·104, the goods should be rejected as adulterated.”

In this connection, it may be remarked that these values do not agree at all well with those formed by Beckurts and Brüche. The examination of a large number of commercial varieties would indicate that no reliable conclusions can be based on the sp. gr. of storax as a guide to purity, in view of the original percentage of water in the substance or the saline content of that water.

¹ What becomes of the volatile constituents? Can the final product still be regarded as storax?

Evers carried out further researches, and recommended the iodine value for detecting adulteration. For purified dehydrated storax he found—

From extract	Sp. gr.	1·119	1·117	1·119	1·120
	Acid value, d. (S.-Z. d.)	52·2	56·7	—	—
	Ester value (E.-Z.) .	184·2	173·5	—	—
	Saponification value, h. (V.-Z. h.) .	236·4	230·2	—	—

On this point the author has already expressed himself as follows:—

“Evers has recently spoken in favour of the iodine value determination for storax. However, as he did not succeed in detecting adulterations by the iodine value, only moderate importance can be attached to this constant, since the acid and saponification values suffice for identification. As Evers admits, the titration in the iodine value estimation for storax is occasionally very difficult, owing to the formation of dark precipitates, which ball together and occlude iodine.

“Moreover, Evers only examined two adulterated specimens (containing castor oil and turpentine), whereas other adulterations, such as with benzol, Tolu balsam, colophony, resin oils, etc., ought also to be tested. The advocated iodine value, however, as the figures show, did not prove suitable for detecting the aforesaid adulterations; and, as a means of identification, is hardly necessary, being replaced by the acid, ester, and saponification values.

“It must also be admitted that, when an alcoholic extract is used, the liquids obtained in testing, not only for the iodine value, but also for the acid, ester, and saponification values, are very difficult to titrate, and, above all, prevent the accurate detection of the colour-change.”

In order to obtain values which shall correspond in all cases to the unaltered drug, and afford a basis for

valuing the commercial product, the author recently examined some perfectly pure specimens of storax—authentic, and taken direct from the parent tree,—various samples of the commercial product being also tested for the sake of comparison.

The method worked out by the author has mainly in view the employment of an unfiltered alcoholic solution of crude storax, instead of the extracts used hitherto, and the production of a light coloured, easily titrated saponification liquid by the cold process. The method was based on the results of numerous preliminary experiments, which need not be detailed here.

The following results were obtained in the comparative experiments between the crude products and the extract:—

I. The unaltered drug—

Acid value, d. (S.-Z. d.)	49·045	50·053
Saponification value, cold (V.-Z. k.)	156·726	157·460

II. Alcoholic extract.—The values refer to 1 gram. of extract, not 1 gram. of crude product—

Acid value, d. (S.-Z. d.)	55·040	56·297
Saponification value, cold (V.-Z. k.)	194·300	194·565

III. Alcoholic extract.—The values refer to 1 gram. of crude product—

Acid value, d. (S.-Z. d.)	40·208	40·873
Saponification value, cold (V.-Z. k.)	141·913	142·122

From these experiments it is evident that—

(a) The values obtained from, and calculated to, extract are much higher than those from the crude product, since they correspond to more than 1 gram. of the initial material.

The values so obtained, therefore, cannot be considered as on a par with the saponification values of the crude product, or serve as a criterion for the latter.

(b) The values obtained with the extract, and then calculated to 1 grm. of crude product, are much lower than those from the crude drug itself, owing to the loss of volatile matter during the preparation of the extract.

(c) As a general rule, none of the values furnished by the extract agree with those yielded by the crude drug, nor can they serve as a basis for conclusions upon the latter; indeed, the figures obtained from the crude product are alone suitable as a guide to the valuation of same.

The author's method is as follows:—

(a) *Loss at 100° C.*—Two grms. of storax are dried at 100° C. in the oven until of constant weight.

(b) *Determining the soluble in alcohol.*—Ten grms. of storax are weighed into a 200 c.c. beaker and dissolved by warming in 100 c.c. of 96 per cent. alcohol, then passed through a dry, tared filter into a tared porcelain basin, the beaker and filter being washed with 50 c.c. of hot alcohol. The filtrate is concentrated by evaporation, and the residue dried at 100° C. till constant. It is advisable to weigh along with the basin a small glass rod, which serves to stir the resinous residue during drying. To prevent the troublesome creeping which occurs during the evaporation of resin solutions, it is advisable to float the porcelain basin in a larger basin of water, instead of setting it direct on the water bath or steam bath. The resin solution will then only creep to the same height as the level of the water in the outer basin.

By also drying and weighing the filter and beaker, the percentage of dirt and woody fragments in the sample can be determined.

(c) *Determining the insoluble in alcohol.*—The insoluble residue from the preceding estimation is weighed and calculated as a percentage.

(d) *Ash.*—The dried storax from *a* is incinerated and calcined until constant.

(e) *Acid value, direct* (S.-Z. d.).—About 1 gram. of storax is dissolved in 100 c.c. of 96 per cent. alcohol, without heat, and titrated with alcoholic $\frac{n}{2}$ caustic potash and phenolphthalein until the colour changes to red. The number of c.c. of KHO consumed, multiplied by 28.08, gives the acid value.

(f) *Saponification value, cold* (V.-Z. k.).—About 1 gram. of storax is suffused with 20 c.c. alcoholic $\frac{n}{2}$ potash and 50 c.c. of benzine (sp. gr. 0.700) in a 1 litre flask, fitted with ground stopper. After standing for twenty-four hours at room temperature, the contents are titrated back with $\frac{n}{2}$ sulphuric acid, without any addition of water. The volume (c.c.) of combined $\frac{n}{2}$ potash and phenolphthalein, multiplied by 28.08, gives the saponification value.

(g) The *ester value* is found by subtracting the acid value from the saponification value.

It should be noted that the storax must be freed from any mechanically adherent water before it is used for analysis; of course only the water that is to some extent combined in the form of emulsion comes into question for the determination. An extra artificial addition of water, beyond the natural quantity that is left in the boiling, can only be incorporated by proper mixing and emulsification, and not by mere contact as a supernatant stratum.

As it is difficult to weigh out 1 gram. with accuracy in the case of storax, and weighing into a narrow-necked flask is also troublesome, the best method is to take up the drug on the tip of a small glass rod, the whole being then placed together in the flask.

With authentically pure varieties of storax the author obtained the following values:—

Moisture	.	.	.	26.21– 40.97	per cent.		
Ash	.	.	.	0.5 – 0.92		„	cal. to natural drug contain- ing original moisture.
Do.	.	.	.	0.74– 1.25		„	cal. to dry drug.
Soluble in alcohol	.	.	.	57.14– 65.49		„	cal. to natural drug.
Do.	do.	.	.	88.75–100.20		„	cal. to dry drug.
Insoluble in alcohol	.	.	.	1.45– 2.61		„	cal. to natural drug.
Do.	do.	.	.	1.97– 3.85		„	cal. to dry drug.
Acid value, d. (S.-Z. d.)				59.38– 70.70			cal. to natural drug.
Do.	do.			87.62– 95.81			cal. to dry drug.
Ester value (E.-Z.)	.	.	.	35.42– 74.43			cal. to natural drug.
Do.	do.	.	.	49.84–109.83			cal. to dry drug.
Sapon. val., c. (V.-Z. k.)				104.67–135.36			cal. to natural drug.
Do.	do.			145.62–199.74			cal. to dry drug.

The numerous commercial varieties examined gave the following values:—

Moisture	.	.	.	19.58– 31.95	per cent.		
Ash	.	.	.	0.24– 3.64		„	cal. to natural drug.
Do.	.	.	.	0.57– 4.75		„	cal. to dry drug.
Soluble in alcohol	.	.	.	64.90– 77.17		„	cal. to natural drug.
Do.	do.	.	.	89.62– 99.63		„	cal. to dry drug.
Insoluble in alcohol	.	.	.	1.66– 7.33		„	cal. to natural drug.
Do.	do.	.	.	2.45– 9.56		„	cal. to dry drug.
Acid value, d. (S.-Z. d.)				38.22– 72.29			cal. to natural drug.
Do.	do.			54.96–106.23			cal. to dry drug.
Ester value (E.-Z.)	.	.	.	47.81–110.03			cal. to natural drug.
Do.	do.	.	.	72.82–142.47			cal. to dry drug.
Sapon. val., c. (V.-Z. k.)				111.89–187.76			cal. to natural drug.
Do.	do.			170.41–233.40			cal. to dry drug.

On comparing these two sets of figures it will be seen that—as in the case of Peruvian balsam—nearly all the commercial kinds are adulterated, impure, or of low quality. To apply the standards obtained by the pure drug to the commercial kinds would practically boycott nearly all the latter. In order to obtain some idea what limits of requirement to prescribe, the author adulterated pure specimens of the drug and examined the products, the results being given in the subjoined table:—

Adulteration of *Styrax liquidus crudus*.

a = calculated to natural drug. b = calculated to dried drug.

Authentically pure <i>Styrax liquidus crudus</i> .	Moisture %	Ash %		Sol. in Alcohol %		Insol. in Alcohol %		Acid Value, d. (S.-Z. d.).		Ester Value (E.-Z.).		Sapon. Value, cold (V.-Z. k.).	
		a	b	a	b	a	b	a	b	a	b	a	b
+ 20 % of Olive oil . . .	33.73	0.62	0.94	63.87	96.38	1.63	2.46	53.65 58.55	80.96 88.35	72.98 68.52	110.12 103.39	126.63 127.07	191.08 191.74
+ 30 % do.	28.22	0.47	0.65	70.59	98.34	1.25	1.74	53.08 55.73	73.95 77.64	78.34 80.87	109.14 112.68	131.42 136.60	183.09 190.32
+ 20 % of Castor (<i>ricinus</i>) oil .	33.96	0.51	0.77	64.72	98.00	1.32	2.00	57.21 58.41	86.63 88.45	66.84 66.78	101.21 101.12	124.05 125.19	187.84 189.57
+ 30 % do. do.	29.30	0.33	0.47	69.65	98.52	0.94	1.32	51.31 52.36	72.57 74.06	79.88 78.95	112.98 111.67	131.19 131.31	185.55 185.73
+ 20 % of ordinary Turpentine .	39.56	0.61	1.01	59.30	98.11	1.17	1.94	78.40 79.62	129.72 131.73	29.53 37.16	48.86 61.48	107.93 116.78	178.58 193.21
+ 30 % do. do.	34.62	0.53	0.81	63.36	96.91	1.10	1.68	84.04 84.43	128.54 129.14	23.01 23.01	35.20 35.20	107.05 107.44	163.74 164.34

These figures show that the added extraneous substances have all modified the values of normal storax, the fatty oils having reduced the acid value, but raised the ester and saponification values; whilst turpentine, on the other hand, depresses the ester value, and, as already shown by E. Dieterich, considerably raises the saponification value. Nothing abnormal is discernible in the other values; consequently the acid, ester, and saponification values, and, in addition, the determination of the percentage soluble in alcohol, are all factors capable of affording useful indications as to the quality of storax.

On the basis of the results furnished by the pure specimens, and in the above experiments with adulterants, the author has proposed the following limits as being not too stringent, whilst, at the same time, they are so drawn as to permit the detection of any considerable degree of adulteration:—

1. Moisture: not to exceed 30 per cent.
 2. Ash: not more than 1 per cent.
 3. Soluble in alcohol: not below 60 per cent. (the former limit of 70 per cent. appears too high).
 4. Insoluble in alcohol: not to exceed 3 per cent.
 5. Acid value, d. 55- 75
 6. Ester value 35- 75
 7. Saponification value, cold 100-140
- } in round numbers.

He is, however, of opinion that further experience is necessary to show whether these values, especially the three last-named constants, are justified.

Gregor and Bamberger gave the following:—

	Methoxyl Value (M.-Z.)—	
	I.	II.
Gregor.	4·5	3·6
Bamberger	0·0	—

(For the worth of these values, see *Chem. Rev.*, 1898, No. 10.)

II. Purified Storax.—A good deal has been written on the methods of purifying storax, some authors recommending alcohol, benzol, benzine, or petroleum ether, whilst others advocate ether. Mylius, in particular, who has done good work in this connection, advises using petroleum ether so as not to dissolve the inactive resin. Nevertheless, in another place, he says that the mixture of oil and storax should be prepared with castor (*ricinus*) oil, and not olive oil, because the latter precipitates the resin, which is an active ingredient in the liniment. Schlickum and E. Dieterich favoured ether, which, in the author's opinion also, is the only correct method, since it dissolves a large quantity of storax, and is itself so readily evaporated that the loss of the volatile constituents of the storax is reduced to a very low figure. Next in value to this solvent is alcohol, followed by petroleum ether and benzine, benzol coming last.

The author experimented in this connection with the aforesaid authentically pure samples of storax, and found that alcohol dissolved 65 per cent.; ether, 69·5 per cent.; benzine, 56·5 per cent.; and benzol, 64·3 per cent.

The product, purified with alcohol, was dark brown, almost perfectly clear; that with ether, pale, like an emulsion; that with benzine, light yellow and clear; and that with benzol, brown and clear. The analytical values, given below, also show that the ether method is the only correct one, and furnishes a product most nearly approximating to the original material.

With regard to the purification of storax, or the preparation of *Styrax liquidus depuratus*, D. A. III., Krüer has made certain proposals, which are mentioned here, not because they bring any improvement, but because they ask something that must be decidedly rejected in the

interest of the constituents of the storax itself. He wishes to boil the drug over an open fire to drive off water, after which it is strained, and so purified. To boil a resin like storax, that contains so large a percentage of volatile and easily decomposable constituents, is altogether inadmissible, in view of its results.

Though the method may be convenient, it certainly cannot be characterised as *lege artis*. Why should a product of such a "secondary" nature as storax, which has already undergone modification and become different from the natural product, be altered further in an unnecessary manner?

Evers gives the following values for purified storax:—

Sp. gr. at 100° C.	Acid Value, h. (S.-Z. d.).	Saponification Value, h. (V.-Z. h.).	Ester Value (E.-Z.).
1·109	55·7	216·0	160·3
1·109	67·0	216·0	149·0
1·114	61·2	211·5	150·3
1·110	56·0	217·9	161·9
1·110	56·3	222·3	166·0
1·111	62·8	221·3	158·5
1·113	60·2	221·1	160·9
1·110	58·0	218·6	160·6
1·109	57·4	218·9	161·5
1·113	59·0	216·6	157·6
1·111	56·1	221·2	165·1
Average	1·111	59·1	218·3
Limits	1·109–1·114	56·0–67·0	211·5–222·3
			149·0–166·0

These values were obtained by the usual method.

Kremel found—

Acid value, d. (S.-Z. d.)	61·0
Ester value (E.-Z.)	76·0
Saponification value, h. (V.-Z. h.)	137·0

values much lower than those of Evers, though obtained by the same method.

E. Dieterich found—

Acid value, d. (S.-Z. d.) . . .	56.94– 84.00
Ester value (E.-Z.) . . .	105.77–173.00
Saponification value, h. (V.-Z. h.) .	178.45–257.00
Ash	0.00– 0.14%
Loss at 100° C.	5.06– 12.63%
Soluble in petroleum ether . . .	37.54– 58.96%
Insoluble do. do. . . .	37.00– 63.15%

Solubility in—

Alcohol (90 per cent.) . . .	almost to completely soluble.
Ether	93.14 per cent. to completely soluble.
Chloroform	almost to completely soluble.
Acetic ether	completely soluble.
Benzol	95.75 per cent. to almost completely soluble.
Petroleum ether	38.18–62.18%
Oil of turpentine	81.80–99.55%
Carbon di-sulphide	86.80–93.39%
} soluble.	

The acid, ester, and saponification values were found by the method used by Kremel.

As already stated, the author has also examined purified storax and obtained standard values for the authentically pure kinds in the purified condition. The method used was that already described under *Styrax crudus*.

The following limits were obtained with authentically pure, unadulterated storax, ether being used to purify the preparations :—

Water	15 per cent.	
Ash	0.03	„ cal. to undried prepn.
Do.	0.04	„ „ dried „
Acid value, d. (S.-Z. d.) . . .	85.97– 88.51	„ undried „
Do. do.	101.73–104.73	„ dried „
Ester value (E.-Z.) . . .	52.11– 52.26	„ undried „
Do. do.	61.66– 61.84	„ dried „
Saponification val., c. (V.-Z. k.)	138.23–140.62	„ undried „
Do. do.	163.57–166.39	„ dried „

Under the same method a number of commercial varieties gave the following values:—

Water	5.91– 10.35%				
Ash	0.01– 0.47%	cal. to undried	prepn.		
Do.	0.01– 0.52%	„	dried	„	
Acid value, d. (S.-Z. d.)	.				59.69– 95.06	„	undried	„	
Do.	do.	.			63.45–116.15	„	dried	„	
Ester value (E.-Z.)	.				54.07–129.44	„	undried	„	
Do.	do.	.			66.08–137.27	„	dried	„	
Saponification val., c. (V.-Z. k.)					148.16–192.61	„	undried	„	
Do.		do.			181.05–208.66	„	dried	„	

As in the case of the crude products, considerable divergencies exist between the normal samples and the purified commercial grades, a matter of small wonder in view of the differences in the composition of the initial materials.

On the basis of the foregoing experience, the author proposes the following limits for the different constants:—

Water : maximum 15 per cent. (the former limit of 8 per cent. seems too strict).

Ash :	„	0.5	„		
Acid value, d. (S.-Z.-d.)	.	.	.	70–90	} in round numbers.
Ester value (E.-Z.)	.	.	.	50–120	
Saponification value, cold (V.-Z. k.)	.	.	.	135–180	

It must be left to the future and to wider experience to determine whether these limits are too strict or too lax. In comparison with normal storax, it is the author's opinion that they are too wide, although it should be borne in mind that if the requirements were made too stringent nearly all the purified commercial grades would fail to pass.

III. *Styrax crudus colatus*.—Under this name there exists in commerce a product that has been freed, as far as possible, from dirt, wood, resin, and water by straining. As the constants have been ascertained, they may be reproduced here.

E. Dieterich found :—

From extract	Acid value, d. (S.-Z.-d.) . . .	63·03– 88·04
	Ester value (E.-Z.) . . .	139·02–140·99
	Saponification value, hot (V.-Z. h.)	203·13–227·16

by the usual method.

The author found, for *S. crudus colatus* prepared from commercial varieties—

Loss at 100° C.	27·00–34·75 per. cent.
Ash	0·00– 1·02 „
Soluble in alcohol	66·4 „
Insoluble in alcohol	2·1 „

He also made a preparation of this kind from the authentically pure specimens of storax already mentioned, and examined the same in an unextracted condition by the method detailed under *S. liquidus crudus*, with the following results :—

Water	37·83 per cent.		
Ash	0·57 „	cal. to undried	prepn.
Do.	0·92 „	„	dried „
Soluble in alcohol	60·83 „	„	undried „
Do. do.	97·84 „	„	dried „
Insoluble do.	1·19 „	„	undried „
Do. do.	1·94 „	„	dried „
Acid value, d. (S.-Z. d.)	70·18– 70·89 „	„	undried „
Do. do.	110·03–112·88 „	„	dried „
Ester value (E.-Z.)	35·91– 39·74 „	„	undried „
Do. do.	57·76– 63·49 „	„	dried „
Saponification val., h. (V.-Z. h.)	106·09–110·36 „	„	undried „
Do. do.	170·64–177·52 „	„	dried „

With regard to the method of heating employed in the preparation of *S. crudus colatus*, the same remarks apply as in the case of Krüer's method of purifying storax.

(For a discussion on the German Pharmacopœia tests for storax, see *Ph. C.*, 1898, No. 20.)

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38. Tacamahac.

Resina Tacamahaca.

Origin and Habitat.—American and West Indian tacamahac comes from *Icica heptaphyllum* and *Elaphyrum tomentosum* (Burseraceæ) ; East Indian tacamahac, from *Calophyllum inophyllum* ; Bourbon tacamahac, from *C. Tacamahaca* (Burseraceæ). Usually the origin is uncertain. East Indies, Mascarenes, America.

Chemical Constituents.—The composition is similar to elemi and anime, but has not been more closely investigated.

General Properties and Commercial Varieties.—Tacamahac is generally called “ West Indian anime ” ; nevertheless, anime (*q.v.* and under Elemi) is a decidedly distinct, though similar, resin.

East Indian tacamahac (*alba, orientalis*) is a yellowish grey-brown, semi-transparent, soft, and sticky resin, with greasy lustre, an aroma of lavender, and bitter spicy flavour.

Bourbon tacamahac (“ Marienbalsam ”) is a soft, dark bluish green, sticky resin, smelling rather like *Fœnum græcum*, and only partly soluble in alcohol. It has been considered as identical with Caranna resin (*q.v.*), an opinion that has, however, been questioned of late.

American tacamahac (*occidentalis*) is a solid resin, consisting of different size lumps, somewhat transparent, brown,

easily crumbled, with a smooth, lustrous fracture. At the present time, *Tacamahaca alba* is the sole commercial variety. A similar resin, from *Calophyllum Calaba*, is known as "*Resina ocuye*," but is not met with in commerce.

Adulterants.—*Resina anime*, various grades of elemis, and other allied and similar resins.

Analysis.—Hirschsohn examined the portion soluble in hot petroleum ether, and dried at 120° C., with the following results :—

Tacamahaca orientalis	.	.	44.11 per cent.	} soluble.
Blackish grey tacamahac	.	.	52.93	
Do.	do.	.	26.99	
Tacamahaca Mexicana	.	.	69.64	

E. Dieterich determined the iodine value (= 70.93—77.72) of *Tacamahaca alba*; and the author obtained the subjoined values during a recent examination of several kinds :—

	Acid Value, d. (S.-Z. d.).	Ester Value. (E.-Z.).	Saponification Value, h. (V.-Z. h.).
Bourbon tacamahac	{ 38.10	68.22	106.32
	{ 39.06	78.47	117.53
West Indian do.	{ 28.40	68.43	96.83
	{ 22.71	75.88	98.59
Do. do.	{ 20.39	77.33	97.72
	{ 27.75	95.15	122.90
East Indian do.	{ 32.99	38.81	71.80
	{ 34.43	36.57	71.00
Do. do.	{ 21.41	32.67	54.08
	{ 21.37	37.58	58.95
Do. do.	{ 22.20	60.90	83.10
	{ 22.60	66.31	88.91

As tacamahac resins are very impure, and probably more or less artificial preparations, the fluctuations exhibited by the several kinds need cause no surprise. It is note-

worthy that the East Indian kinds furnish lower values than those from the West Indies.

All the above figures were obtained by the usual method. The values previously obtained by the author with the cold saponification process (20–50) are untenable, tacamahac being unsaponifiable in the cold. At that time there were no other figures available for comparison.

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39. Thapsia Resin.

Resina Thapsiæ.

Origin and Habitat.—*Thapsia garganica*, L. (Umbelliferae). North Africa, Southern Europe.

Chemical Constituents.—The plant contains a milky sap, which furnishes a non-nitrogenous, blistering substance, crystallising in small plates, and melting at 87° C.; caprylic acid and dibasic thapsic acid ($C_{16}H_{30}O_4$) are also present. The active, French commercial extract from the root contains thapsic acid, ethereal oil, 66 per cent. of resin, euphorbon, cholesterin, ischolesterin, gum, fat, aliphatic acids, a terpene which boils at 180° C., a camphene boiling at 170° C., and water. The euphorbon may originate in an admixture of euphorbium (Canzoneri).

General Properties and Commercial Varieties.—The resin from the plant or root is a dark, opaque, turbid extract, generally containing water. It has a highly disagreeable smell, and is for the most part soluble in alcohol, carbon di-sulphide, chloroform, and ether, but only partly so in benzine and petroleum ether.

Water and alcohol are generally employed for the extraction, and additions of extract from *Thapsia villosa* and euphorbium are also made. The extract from *T. villosa* also contains acrid substances soluble in petroleum ether, but is milder in its action than that from *T. garganica*.

The pure French commercial grades act more rapidly than those found in the German market.

Adulterants.—Inferior resins devoid of stimulating properties, euphorbium, and resin from *T. villosa*.

Analysis.—Apart from various reports on the admixture of the less effectual resin from *T. villosa* and of euphorbium, there are practically no analytical data available on Thapsia resin.

It was not until recently that the investigation of Thapsia resin was undertaken by the author, and a method elaborated which, on the one hand, enables the operation to be carried on in safety, and, on the other hand, has given materials for the first foundations of a system of valuing and judging the product.

As even the mere heating or evaporating of a Thapsia solution, etc., entails great danger to the operator—extremely painful itching inflammation—the author has borne this in mind, and avoided in his method working with hot liquids or evaporating, except under suitable precautions.

The method comprises—

- (a) Estimating the percentage soluble in petroleum ether.
- (b) Hot saponification value of this portion, referred to 1 gram.
- (c) Estimating the percentage soluble in alcohol.
- (d) Estimating the percentage insoluble in alcohol.
- (e) Hot saponification value of the portion soluble in alcohol, referred to 1 gram.
- (f) Total hot saponification value of the original resin.

(g) Percentage of water.

(h) Ash content.

About 1 gram. of Thapsia resin is mixed with a sufficient amount of pure sand, and the crumbled mass placed in a Schleicher and Schüll cartridge, the weight of cartridge + sand + resin being noted, as well as that of the cartridge + sand, and of the resin by itself. The whole is then treated, in a Soxhlet extractor, with petroleum ether for three hours, and, after cooling down, the cartridge is dried in the oven at 80° C. until no further odour of petroleum ether is discernible; longer drying must be avoided in view of the moisture-content of the resin. The cold petroleum ether extract is next treated with 20 c.c. of alcoholic $\frac{n}{2}$ caustic potash and boiled for half an hour under a reflux condenser, the apparatus being tightly stoppered. After cooling, the *saponification value of the portion soluble in petroleum ether* is determined by the usual method (see Introduction to Part II.), and the results are referred to 1 gram.

The percentage soluble in petroleum ether is found, indirectly, by calculation, from the loss in weight of the aforesaid cartridge, and expressed as a percentage. The cartridge is then replaced in the extractor, and, after charging the bottom flask with 20 c.c. of alcoholic $\frac{n}{2}$ caustic potash and 50 c.c. of alcohol, is extracted for two hours longer. The alcohol serves as the extracting reagent, whilst the underlying alkali immediately saponifies the dissolved substances. After two hours the whole apparatus is cooled, and the cartridge is then dried at 100° C. until constant.

The extra loss in weight, calculated in percentages, gives the value of the *portion soluble in alcohol*; the residue, which is easily calculated by deducting the weight of cartridge + sand from the total weight of cartridge + sand + resin, expresses the value, *insoluble residue*.

The saponification liquid in the flask is titrated and—calculated to 1 grm.—gives the *saponification value (hot) of the portion soluble in alcohol*.

The *total saponification value (hot)* of the original resin is found by saponifying 1 grm. of the resin with 25 c.c. of alcoholic $\frac{n}{2}$ potash, under a reflux condenser, and titrating back when cold.

The percentage of the moisture and ash are determined by known methods, with the precaution, however, that a properly ventilated drying cupboard is used, the draught pipe of which discharges into the open air (this is easily effected by means of rubber piping and glass tubing). The bulk of the active ingredients is in the portion soluble in petroleum ether, only small quantities being found in that soluble in alcohol.

Several commercial varieties, chief among them being three pure French resins, and two inferior German commercial specimens, gave the values recorded in the following table:—

[TABLE

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
Thapsia Resin.	Water %	Ash %	Soluble in Petroleum Ether %	Sapon. Val., h., of No. 5, cal. to 1 grm.	Soluble in Alcohol %	Sapon. Val., h., of No. 5, cal. to 1 grm.	Residue insoluble in Alcohol %	Total Sapon. Val., h., of Crude Res.
No. I. Pure, of French origin, very strong—								
Cal. to undried drug . . .	10.336	0.403	23.02	225.90	74.83	340.17	2.15	$\left\{ \begin{array}{l} 301.57 \\ 326.99 \end{array} \right.$
Do. anhydrous drug . . .	—	0.450	25.67	251.94	83.46	379.38	2.40	$\left\{ \begin{array}{l} 336.33 \\ 364.68 \end{array} \right.$
No. II. Pure, French, very strong—								
Cal. to undried drug . . .	7.916	0.415	17.75	332.60	82.25	338.74	0.00	$\left\{ \begin{array}{l} 317.55 \\ 333.24 \end{array} \right.$
Do. anhydrous drug . . .	—	0.451	19.28	360.18	89.32	367.86	0.00	$\left\{ \begin{array}{l} 344.84 \\ 361.88 \end{array} \right.$
No. III. Pure, of French origin—								
Cal. to undried drug . . .	7.43	0.16	19.73	282.83	72.81	375.42	0.199	$\left\{ \begin{array}{l} 353.68 \\ 355.89 \end{array} \right.$
Do. anhydrous drug . . .	—	0.173	21.31	305.53	86.71	405.55	0.215	$\left\{ \begin{array}{l} 383.07 \\ 384.47 \end{array} \right.$
No. IV. Origin doubtful, less strong—								
Cal. to undried drug . . .	32.38	0.388	$\left\{ \begin{array}{l} 42.45 \\ 44.03 \end{array} \right.$	$\left\{ \begin{array}{l} 114.38 \\ 113.04 \end{array} \right.$	$\left\{ \begin{array}{l} 56.67 \\ 53.78 \end{array} \right.$	$\left\{ \begin{array}{l} 383.80 \\ 384.41 \end{array} \right.$	$\left\{ \begin{array}{l} 0.88 \\ 2.19 \end{array} \right.$	$\left\{ \begin{array}{l} 255.11 \\ 265.17 \end{array} \right.$
Do. anhydrous drug . . .	—	0.574	$\left\{ \begin{array}{l} 62.78 \\ 65.12 \end{array} \right.$	$\left\{ \begin{array}{l} 169.15 \\ 167.17 \end{array} \right.$	$\left\{ \begin{array}{l} 83.81 \\ 79.35 \end{array} \right.$	$\left\{ \begin{array}{l} 567.59 \\ 568.49 \end{array} \right.$	$\left\{ \begin{array}{l} 1.30 \\ 3.24 \end{array} \right.$	$\left\{ \begin{array}{l} 377.78 \\ 392.15 \end{array} \right.$
No. V. Origin doubtful, obtained from a German firm. Poor—								
Cal. to undried drug . . .	9.032	0.380	$\left\{ \begin{array}{l} 38.22 \\ 42.02 \end{array} \right.$	$\left\{ \begin{array}{l} 249.21 \\ 236.59 \end{array} \right.$	—	$\left\{ \begin{array}{l} 335.54 \\ 341.72 \end{array} \right.$	—	290.76
Do. anhydrous drug . . .	—	0.418	$\left\{ \begin{array}{l} 42.02 \\ 46.19 \end{array} \right.$	$\left\{ \begin{array}{l} 273.96 \\ 260.08 \end{array} \right.$	—	$\left\{ \begin{array}{l} 368.86 \\ 375.65 \end{array} \right.$	—	319.63

These values furnish the subjoined maximum, minimum, and mean values for the *pure*, active resin, calculated to the anhydrous drug—

	I.	II.	
	Maximum and Minimum Limits.	Mean.	Or in Round Numbers.
Water	7.43– 10.336 %	8.88 %	9 %
Ash	0.16– 0.415 %	0.2875 %	0.3 %
Soluble in petroleum ether	19.28– 25.67 %	22.475 %	22.5 %
Sapon. val., h., of same, cal. to 1 grm.	251.94–360.18	306.06	305
Soluble in alcohol	83.46– 89.32 %	86.39 %	86.5 %
Sapon. val., h., of same, cal. to 1 grm.	367.86–405.55	386.05	386
Residue insoluble in alcohol . . .	0.00– 2.40 %	1.2 %	—
Total saponification value, h. . .	336.33–384.47	360.40	360

In contrast to these figures No. IV. in the table shows an abnormally high percentage of water, and a very high percentage soluble in petroleum ether, with a very low saponification value, h. (V.-Z. h.) for same; resin No. V. shows a very high percentage soluble in petroleum ether, with a low saponification value, h., for same, as also a very low total saponification value, h. Although, on the basis of these researches, the author does not venture to assume that there is any direct connection between these abnormal values and the activity of the corresponding resins, he nevertheless considers it advisable to give special prominence to these divergent and fluctuating figures, and contrasts them with the relatively harmonious values of the pure and efficacious specimens of Thapsia resin, which vary within restricted limits only.

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40. Turpentine.

Terebenthina, *Balsamum Terebinthinae* (official in Germ. Pharm. III.).

I. ORDINARY TURPENTINE.

Origin and Habitat.—Numerous varieties of *Pinus*, such as *P. pinaster*, *P. Laricio*, etc. (Abietineæ). Europe.

Chemical Constituents.—Abieto-pimaric acid, water, oil of turpentine, and bitter principle. Tschirch has recently isolated new “crystalline resinol acids” from the resins from *Pinus palustris*, *Picea vulgaris*, *Abies pectinata*, by fractional separation (see *Ph. Ztg.*, 1899, No. 77).

II. LARCH-VENICE TURPENTINE.

Origin and Habitat.—*Larix decidua*, M. (Abietineæ). Europe.

Chemical Constituents.—Ethereal oil, $C_{10}H_{16}$ (15–20 per cent.), caffeic acid, vanillin, ferulaic acid (?), abietic acid, water, bitter principle, formic acid. Tschirch has recently isolated new “crystalline resinol acids” from the resin from *Larix decidua* by fractional separation (see *Ph. Ztg.*, 1899, No. 77).

General Properties and Commercial Varieties.—The ordinary turpentine is thin (to thick) flowing, crystalline, with a strong smell of oil of turpentine, and setting hard immediately in contact with calcium hydroxide (2 parts to 10 of turpentine). Whereas the ordinary turpentines are of balsamic consistence, the pine resins—*Resina Pini* (*q.v.*), which is also obtained from varieties of *Pinus*—are more solid.

Venice turpentine is almost perfectly clear; it does not become crystalline, nor does it set immediately when mixed with calcium hydroxide.

Strassburg turpentine, from *Pinus picea* (*Abies pectinata*), is thin, clear, yellow, and slightly fluorescent.

Chios turpentine is like mastic (*q.v.*), and comes from species of *Pistacia*.

Russian turpentine, from *Pinus sylvestris*, contains, according to Schkatelow, 30 per cent. of a dry, crystalline acid ($C_{40}H_{58}O_5$).

Canada balsam and *Mecca balsam* (*q.v.*) are also turpentines in the wider sense of the term. (For *Terebinthina cocta*, see *Resina Pini*.) A turpentine of sharp, acrid flavour, and containing succinic and abietic acid is furnished, according to Hartwich, by the Mexican *Pinus religiosa* (*Abietineæ*) and is known as "Aceite de abeto." *Carpathian balsam*, or *Balsamum Carpathicum*, comes from *Pinus Cembra*, L.

Adulterants and Substitutes.—Artificial mixtures of resin, oil of turpentine, and water.

Analysis.—The chief varieties that have been subjected to analytical examination are Chios turpentine, ordinary turpentine from various sources, Venice turpentine, and Russian turpentine. Artificial commercial products have also been tested, and Strassburg turpentine, Canada balsam, and Mecca balsam (*q.v.*) have been described. The reason why the turpentines are not included with the balsams in the present work, as is oftentimes done, is that, instead of being solutions of resins in ethereal oils like most of the balsams, the turpentines are very thick and viscid mixtures, which are partly crystalline, and are more nearly allied to the resins than to the balsams, though much softer than the almost perfectly solid pine resins (*q.v.*) met with in commerce. This also applies to storax (*q.v.*).

The analysis of the turpentines will be dealt with in the following order:—

- I. Ordinary turpentines.
- II. Larch turpentine.
- III. Chios turpentine.
- IV. Strassburg turpentine.

I. ORDINARY TURPENTINES.

Hirschsohn found the turpentines dissolve in petroleum ether, except for a slight residue.

Kremel found—

	I.	II.
Acid value, d. (S.-Z. d.)	128·7	124·4

by the usual method. He did not ascertain any other values.

E. Dieterich found—

(a) *Terebinthina communis* (*Abietina*)—

Acid value, d. (S.-Z. d.)	112·45–136·81
Ester value (E.-Z.)	9·84– 32·75
Saponification value, h. (V.-Z. h.) . .	139·77–160·93

(b) *Terebinthina communis* (*Gallica*)—

Acid value, d. (S.-Z. d.)	104·72–140·93
Ester value (E.-Z.)	2·80– 9·80
Saponification value, h. (V.-Z. h.) . .	108·99–149·33

Solubility in—

Alcohol (90 per cent.)	complete.
Ether	„
Chloroform	„
Acetic ether	„
Benzol	„
Oil of turpentine	„
Carbon di-sulphide	almost complete.
Petroleum ether	94·04–95·71 %

(c) *Terebinthina communis* (*Pinus Cembra*)—

Acid value, d. (S.-Z. d.) . . .	117·03–118·56
Ester value (E.-Z.) . . .	56·01– 60·19
Saponification value, h. (V.-Z. h.) .	167·40–179·53

(d) *Terebinthina communis* (*Pinus sylvestris*)—

Acid value, d. (S.-Z. d.) . . .	128·65–144·94
Ester value (E.-Z.) . . .	34·59– 38·75
Saponification value, h. (V.-Z. h.) .	167·40–179·53

All these values were determined by the usual method, except that the saponification liquid was first evaporated, and then taken up again with alcohol for back titration.

K. Dieterich found—

	I.	II.	III.	IV.
Acid value, d. (S.-Z. d.) . . .	107·98	107·69	112·42	113·36
Ester value (E.-Z.) . . .	10·02	7·82	17·25	20·39
Saponification value, h. (V.-Z. h.)	118·00	115·51	129·67	133·65

and later—

	I.	II.	III.	IV.	V.
Acid value, d. (S.-Z. d.)	112·93	115·13	115·32	114·84	115·88
Ester value (E.-Z.) .	7·77	6·30	7·15	4·29	4·14
Sapon. val., h. (V.-Z. h.)	120·70	121·43	122·47	119·13	120·02

also by the usual method—

Dietze found with French turpentine—

Acid value, d. (S.-Z. d.) . . .	119·67–120·41
Ester value (E.-Z.) . . .	1·76– 3·05
Saponification value, h. (V.-Z. h.) .	121·43–123·46

These values (also obtained by the usual method) agree well with those found by E. Dieterich (see above, *T. communis Gallica*).

Kitt determined the carbonyl value of resin from *Pinus halepense*, and found—

	I.	II.
Carbonyl value (C.-Z.) . . .	0·28	0·57

The author examined the acetyl values for ordinary turpentine, with the following results :—

Acetyl	{ Acid value (A.-S.-Z.)	123·75–125·55
	{ Ester value (A.-E.-Z.)	62·32– 93·79
	{ Saponification value (A.-V.-Z.)	187·87–217·04

the acetylated product being solid, though the original substance is viscid.

(For the worth of the carbonyl and acetyl values, see *Chem. Rev.*, 1898, No. 10.)

The chief distinction between ordinary and Venice turpentine is in the higher acid value of the former. Schkatelow has reported on the chemical data of the above-mentioned Russian turpentine from *Pinus sylvestris* (see the values given by E. Dieterich, under *d*), but not on the analytical details. As a rule, all the pine (*Pinus*) turpentines give the same values, and are distinguishable solely by their outward appearance, their solubility in ether and alcohol being almost identical.

In contrast to colophony, which forms the distillation residue from turpentine, all the turpentines and pine resins (*q.v.*) contain ester compounds, which pass over, either as such or in the form of decomposition products, on distillation, leaving colophony (*q.v.*) behind as an ester-free but etheriferous and lactoniferous resin, with or without traces of ethereal oil.

(For the German Pharmacopœia (III.) tests for turpentine, see *Ph. C.*, 1898, No 20.)

II. LARCH TURPENTINE.

Being a more valuable product, Venice turpentine has been more closely investigated than ordinary turpentine, and the analytical values obtained harmonise very well and are fairly exact.

Hirschsohn found that larch turpentine is almost completely soluble in petroleum spirit.

A. Kremel found—

	I.	II.
Acid Value, d. (S.-Z. d.)	68.4	70.3

by direct titration, but did not determine the ester and saponification values.

Von Schmidt and Erban found—

Acid value, d. (S.-Z. d.)	67.7
Ester value (E.-Z.)	29.8
Saponification value, h. (V.-Z. h.)	97.5

all by the usual method.

Solubility in—

Alcohol	} complete.
Ether	
Methyl alcohol	
Amyl alcohol	
Benzol	} complete.
Petroleum ether—almost complete.	
Acetone	
Glacial acetic acid	
Chloroform	} complete.
Carbon di-sulphide—partial.	
Oil of turpentine—complete.	

Beckurts and Brüche found—

	I.	II.	III.	IV.	V.	VI.	VII.
Sp. gr.	1.091	1.121	1.160	1.100	1.180	1.190	1.060
Acid value, d.							
(S.-Z. d.)	85	76	81	94	101	98	93
Ester value (E.-Z.)	9	5	0	3	0	0	6
Sapon. value, h.							
(V.-Z. h.)	85	81	81	97	101	98	99

the three latter values by the usual method.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	64.44– 76.69
Ester value (E.-Z.)	35.41– 55.94
Saponification value, h. (V.-Z. h.)	108.27–132.63

Solubility in—

Alcohol (90%)	} complete.
Chloroform	
Acetic ether	
Benzol	
Oil of turpentine	} complete.
Carbon di-sulphide	
Petroleum ether	
Ether	

In determining the saponification value the liquid was evaporated, taken up again with alcohol, and then titrated. The acid value was found by direct titration of the alcoholic solution. The solubilities agree with those of von Schmidt and Erban (see above).

The author found—

Acid value, d. (S.-Z. d.)	66.93– 68.85
Ester value (E.-Z.)	46.27– 54.94
Saponification value, h. (V.-Z. h.)	114.56–127.71

by the usual method; the figures agree well with those found by other authors.

He also examined the acetyl values of Venice turpentine, and found—

Acetyl	Acid value (A.-S.-Z.)	69.87– 72.19
	Ester value (A.-E.-Z.)	109.08–118.67
	Saponification value (A.-V.-Z.)	178.95–190.86

Both Gregor and Bamberger obtained negative results with the methoxyl value test.

The chief adulterants of larch turpentine are artificial preparations, ordinary pine turpentines, and extraneous resins.

Hoffmann has reported on artificial Venice turpentine which he declares to be a product free from oil of turpentine, and of altogether different behaviour. According to Schaal, an artificial turpentine of this class is prepared, from conifer resins, by distillation *in vacuo* at 270°C ., and subsequent distillation with oil of turpentine under reduced pressure.

E. Dieterich examined an artificial product of this kind, and found—acid value, d., 98·79; ester value, 0·88; saponification value, h., 97·66.

Von Itallie remarks as follows:—

“In the *H. A.*, 1893, E. Dieterich mentions solutions of resin in resin oil, which are sold as *Terebinthina veneta*, and that their acid and saponification values are almost identical, whereas in good sorts of turpentine the acid value is about 70, and the saponification value, 120:

“I received two kinds of turpentine which gave the following values:—

Acid Value, d. (S.-Z. d.).	Saponification Value, h. (V.-Z. h.).
97·0	108·0
99·5	109·3

and were therefore mixtures, consisting mainly of resin and resin oil.”

With regard to the detection of ordinary turpentine in larch turpentine, Hirschsohn says:—

“To detect ordinary turpentine in larch (Venice) turpentine, the Hübl saponification method, recommended by some, is unsuitable, because the acid and ester values thereby obtained vary very considerably, both in the case of ordinary turpentine, and of larch turpentine as well.”

On the other hand, Hirschsohn discovered, in the behaviour

of turpentine towards ammonia, a means said to be not only capable of distinguishing between ordinary and larch turpentine, but also, to some extent, of detecting the presence of the former in the latter.

“When a small quantity of ordinary turpentine is suffused in a test glass with strong ammonia (sp. gr. 0·96), it gradually distributes itself throughout the liquid, as a kind of milk; whereas, if larch turpentine be treated the same way, the liquid remains clear. On attempting to distribute the turpentine through the liquid by means of a glass rod, it is found that larch turpentine apparently remains unchanged at first, as an oily mass in the aqueous liquid, but afterwards is converted into a semi-solid, colourless, opaque mass, the liquid being only slightly turbid; ordinary turpentine, on the other hand, immediately distributes in the form of milk, which soon sets to a jelly, especially when the proportion of turpentine to ammonia is about 1 : 5. Larch turpentine, containing 50 per cent. of ordinary turpentine, readily distributes in ammonia, the mixture solidifying in about five minutes, and clarifying when set in hot water; a mixture containing 30 per cent. of ordinary turpentine also distributes easily, solidifies in about ten minutes, and clarifies in the water bath; with 20 per cent. of ordinary turpentine the sample runs to milk very easily, and does not solidify, but clarifies, on the water bath; when the proportion of ordinary turpentine is less than 20 per cent. it cannot be detected, unless an undoubtedly pure larch turpentine be at hand for comparison.

“Mixtures of larch turpentine with not less than 30 per cent. of ordinary turpentine can be recognised with a fair degree of certainty by means of 80 per cent. alcohol. If 1 part of turpentine be suffused with 3 parts of alcohol and shaken up, larch turpentine gives an almost clear solution,

whereas more than half of the total quantity of ordinary turpentine present separates out in a short time."

Although this method of Hirschsohn is not free from objection, and its indications are in nowise to be considered superior to those of the acid, ester, and saponification values, it may nevertheless find a place here as a confirmatory test in doubtful cases. The importance of the acid, ester, and saponification values is evident from the circumstance that ordinary turpentine has a much higher acid value than Venice turpentine; so that larger additions of ordinary turpentine to the latter may be recognised by these values. The acetyl acid value of ordinary turpentine is also much higher than that of Venice turpentine, which is an interesting fact, and one indicating the worth of the acetyl values. The quantity of the hydroxyl groups, expressed by the acetyl values, therefore turns out greater or smaller according to the amount of the resin acids present containing hydroxyl. The same remarks also apply to the acetyl-ester and acetyl-saponification values. (With regard to the worth of the methoxyl and acetyl values of the resins, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharm. tests for turpentine, see *Ph. C.*, 1890, No. 20.)

III. CHIOS TURPENTINE.

Though Chios turpentine is often erroneously classed with the *Larix* turpentines, it will be treated separately here, because several reports on it are found in the literature of the subject.

According to Wigner, the following requirements should be fulfilled by Chios turpentine:—

"The sp. gr. is 1.050, but varies, like the consistence, with the percentage of volatile oil. The taste is faintly aromatic, like turpentine, and entirely devoid of bitterness or sharpness;

the odour agreeably aromatic, slightly recalling that of turpentine. It is completely soluble in alcohol and ether, only earthy admixtures being left behind. The solution in rectified alcohol is not quite clear, but very little deposit comes down on cooling. An admixture of conifer resins can be detected by the solubility test; and an indication is also afforded when the microscopic examination of the residue reveals the pitted vessels so characteristic of coniferous woods. The optical behaviour of Chios turpentine also serves to distinguish it from other kinds of turpentine, the ethereal oil of the former being strongly dextro-rotatory, whereas the oils of most conifers give a levo-rotation. Conversely, the resins of most conifers are dextro-rotatory, that of Chios turpentine being probably levo-rotatory."

W. Bettink would require Chios turpentine to be completely soluble in boiling alcohol, the solution becoming turbid on cooling. The taste should be neither sharp nor bitter, and the turpentine itself should be devoid of crystals. The mechanical impurities should not exhibit any pitted (conifer) vessels. As this author was in possession of authentic samples, these indications are valuable; above all, the microscopic examination of this turpentine is advisable.

Landerer drew attention long ago to the adulteration of Chios turpentine, and found as much as 20–30 per cent. of sand and stones in the natural product.

Kremel gives the following values for Chios turpentine:—

	I.	II.
Acid value, d. (S.-Z. d.) .	47.8	53.4

by direct titration, but did not determine the saponification value.

E. Dieterich also accurately examined Chios turpentine, and made valuable reports. That he should, however, have

treated Chios turpentine as *Terebinthina Laricina*, whereas it is derived from *Pistaceæ*, cannot be approved. This *Pistacia* turpentine is distinguishable from the *Pinus* and *Larix* turpentines by the absence of the characteristic pitted vessels, and should on no account be classed with the *Larix* turpentines.

E. Dieterich found—

Acid value, d. (S.-Z. d.)	. . .	47·13-48·53
Ester value (E.-Z.)	. . .	19·13-21·47
Saponification value, h. (V.-Z. h.)	. . .	66·26-70·00

Solubility in—

Ether	}	almost to completely soluble.
Chloroform		
Acetic ether		
Benzol		
Oil of turpentine	}	
Alcohol (90 per cent.)	.	98·64 to completely soluble.
Carbon di-sulphide	.	almost completely soluble.
Petroleum ether	.	98·49 per cent. to completely soluble.

IV. STRASSBURG TURPENTINE.

(*Terebinthina argentoratensis*.)

Though actual analytical data for Strassburg turpentine are lacking, and the article itself has now almost entirely disappeared from the market, it is nevertheless included here for the sake of completeness.

According to Flückiger, the resin sap of the white pine agrees perfectly with Canadian turpentine (see Canada balsam), except as regards solubility, the former being miscible in all proportions with glacial acetic acid, absolute alcohol, and acetone, to form a clear liquid. The white pine turpentine has also a finer odour, so that it was formerly

known in France as *Térébinthine au citron*. The taste has not the sharpness of Canada balsam, and is less bitter. No fluorescence is discernible.

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41. Turpethum Resin.

Resina Turpethi.

Origin and Habitat.—*Ipomœa Turpethum*, R. Brown (Convolvulacæ). East Indies.

Chemical Constituents.—The resin "Turpethin" has been said to be identical in composition with Scammonin, but, more correctly speaking, is identical with the Orizabin = Jalapin $C_{34}H_{56}O_{16}$, in Jalapa (Spirigatis). This authority also gives Scammonin as identical with Orizabin = Jalapin, and states that Turpethin is a glucoside of the formula $C_{34}H_{56}O_{16}$.

General Properties and Commercial Varieties.—A brownish yellow, almost inodorous resin, of sharp and bitter flavour; readily soluble in alcohol, but insoluble in ether. The only variety in the market is the resin extracted from the roots, and sold in sticks.

Adulterants.—Vegetable and mineral impurities, and artificial products.

Analysis.—Turpethum resin is prepared in the same manner as Jalapa resin and scammonium, by boiling the roots in water, and recovering the resin by means of alcohol.

It is dealt with in this place mainly because, according to Spirgatis, its constituents are identical with Scammonin and Jalapin. It is sold in sticks, has the melting-point 183° C., and is distinguishable from scammonium and Jalapa resin by its insolubility in ether, wherein the other two are, for the most part, soluble. All three are soluble in alcohol. As with scammonium and Jalapa resin, the ash content should be minimal.

The author has examined the commercial product (*Resina Turpethi* in sticks) by the usual method, and obtained the following values:—

	I.	II.	III.	IV.
Acid value, d. (S.-Z. d.)	20.73	24.45	22.93	20.55
Ester value (E.-Z.)	139.98	137.27	141.01	139.94
Saponification value, hot (V.-Z. h.)	160.71	161.72	163.94	160.49

The various samples, therefore, appear to be fairly uniform in composition.

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C. GUM RESINS.

As was the case with many of the resins, so with the gum resins, the analytical data hitherto accumulated were, almost without exception, obtained with extracts, and consequently are—as already several times remarked—of only relative worth, since the values furnished by extracts can never correspond to those of the crude product, not to speak of their incapacity of affording any reliable evidence on the nature of the latter (see Part I.) Nevertheless, these values obtained from extracts will be recorded for the sake of completeness, since they may be able, in doubtful cases, to at least afford some indication of the characteristics of the gum resin extracts. Moreover, values have already been determined from the unaltered crude product in the case of many of the gum resins. It is worthy of special mention that the values furnished by this class of bodies exhibit the greatest fluctuation shown by any members of the resin product group, a circumstance in part due to the methods employed, and the use of extracts, but mainly to the very changeable constitution of the gum resins themselves, these being the most variable of all the resinous substances so far as concerns the percentage and mutual relation of their contained ethereal oil, gum, resin, etc. Furthermore, the gum resins show the largest percentage (up to 50 per cent.) of ash and impurities, a circumstance which, in conjunction with their greasy character, renders the preparation of an average sample for analysis peculiarly difficult. To triturate the gum resins it is advisable to first cool them down, either in a cold cellar, or, better, in an ice-chest or refrigerating mixture, the appli-

cation of warmth, as recommended by the German Pharmacopœia, being not only unsuccessful and impractical, but also irrational, since it causes a loss of ethereal oil. It is necessary to take four or five samples of each gum resin to be analysed, and to calculate the definite values from the results of four or five analyses. The above remarks as to the use of warmth also apply to the so-called "purified gum resins" (by the wet or dry process) which were formerly plentiful in commerce, though now rare. These extracts, though doubtless practical and also relatively pure, are incapable of corresponding to the crude product, except to a very minor degree. It is therefore worthy of recognition that the German Pharmacopœia has, so far, not acknowledged these products, as the Swiss Pharmacopœia has done with the dry gum resins purified by sifting.

42. Ammoniacum.

Gummi-resina ammoniacum (officinal in Germ. Pharm. III.).

Origin and Habitat.—*Dorema ammoniacum* (Umbelliferae). Persia.

Chemical Constituents.—Matters insoluble in water or alcohol, 3·5 per cent.; acid and neutral resin (total, 60 per cent.). Both kinds of resin are free from sulphur. The acid resin is a salicylic ammoresinotannol ester; and the isolated ammoresinotannol has the formula $C_6H_{10}O$, or $C_{13}H_{29}O_2OH$, so that it is analogous in composition with galboresinotannol (see Galbanum). Ethereal oil (0·2–0·4 per cent.) is also present, and salicylic acid in traces; but no umbelliferon or sulphur. Volatile acids such as acetic and caproic acid are also found (Tschirch & Luz). The gum (12–16 per cent.) is similar to gum arabic, is free from nitrogen, and yields on hydrolysis galactose, arabinose, and mannose (Frischmuth).

General Properties and Commercial Varieties.—

Persian ammoniacum is in the form of greyish white masses, or as tears, yellow externally and white inside. In the cold it is brittle and of peculiar aromatic odour. The variety *in massa* contains more ethereal oil than the *in lacrymis* grade; the former being therefore greasy, whilst the latter is solid. Ammoniacum “in tears” is also the purer kind, but, owing to its lower percentage of ethereal oil, is not superior to the other, for pharmaceutical purposes especially. Persian ammoniacum—which is the only usual commercial quality—is but partially soluble in water or alcohol.

African ammoniacum, from *Ferula tingitana*, bears only a very slight external resemblance to the Persian drug; it is much darker in colour, more impure, and has quite a different taste and smell. Only one grade, *in massa*, appears to exist. It also differs from Persian ammoniacum in giving the umbelliferon reaction with hydrochloric acid and ammonia (see Galbanum), and again by its analytical constants, in which respect it also differs from galbanum.

Adulterants, etc.—Galbanum, African ammoniacum, inferior resins, vegetable detritus, etc.

Analysis.—Frequent reference has been made by various authors to the impurity of ammoniacum, particularly with regard to the ash. E. Dieterich on this account recommended the use of the selected or purified drug, and urged its adoption for the Pharmacopœia. Even, however, if it be possible to reduce the percentage of ash and impurities by purification, the objections mentioned in the Introduction to this Section—and especially those relating to “purified gum resins”—still remain. The Danish Pharmacopœia rightly prescribes that ammoniacum should be powdered in the cooled state (see also Introductory Remarks). Neither the adoption of a purified grade, as advocated by E. Dieterich and Thoms, for

the Pharmacopœia, nor the heating of the product is, however, able to lead to any progress in this connection, the sole remedy being the strict and accurate prescription of the ash content and the percentage soluble and insoluble in alcohol, as frequently urged by the author. The best reactions are those of Picards and Plugge, and, in addition, the author's test as applied to galbanum. Picards found that the alcoholic solution of this gum resin gives a beautiful violet coloration with sodium hypochlorite. Plugge recommends sodium hypobromite, and claims to have detected as low as 1 per cent. of ammoniacum in galbanum and other mixtures. The author, however, has not been able to confirm this; but the samples tested were highly impure kinds, which gave merely dirty, and by no means characteristic, colour shades. Consequently, like other colour reactions, this test can only be considered as of relative value. As has been stated under Galbanum, the detection of ammoniacum in this drug is possible by the quantitative method. Plugge also endeavoured to determine the quantitative presence of ammoniacum in mixtures by means of a standardised solution of bromine. His researches revealed the following constituents in ammoniacum, the figures found by previous authorities being added to the table, for purposes of comparison :—

Constituents.	Plugge.	Buchholz.	Braconnot.	Moss.	Hirschsohn.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Ethereal oil . . .	1·27	} 4·0	} 7·2	} 2·8	1·43- 6·68
Moisture . . .	5·10				0·81- 3·27
Ash . . .	2·00				2·02-16·88
Resin . . .	65·53				47·12-69·22
Gum . . .	26·10	22·4	18·4	19·3	—
Bassorin . . .	—	1·6	—	—	—
Gelatinous substances . . .	—	—	4·4	5·4	—
Extractives . . .	—	—	—	1·6	—
Sugar, etc. . . .	—	—	—	—	1·61- 4·59
Per cent. sol. in water	—	—	—	—	11·85-25·74
Residue . . .	—	—	—	—	0·81- 3·09

Hirschsohn laid down as requirements to be exacted of the Persian grades that the *in massa* mark should contain at least 55 per cent. soluble in petroleum ether, and the *in granis* kind not less than 66 per cent., the ash content being fixed at 3 per cent. (This is a limit which probably only very few *in massa* specimens nowadays exhibit.) The comprehensive researches on ammoniacum have been supplemented by numerous qualitative reactions, one of which enables Persian galbanum to be distinguished from African ammoniacum. As, however, the latter is no longer in the market, it is probable that adulteration is out of the question, owing to the different origin of, and commercial channels traversed by, the two kinds; and, moreover, there is no risk of one being mistaken for the other, their external appearance being distinguishable at the first glance—quite apart from the analytical differences shown by Kremel and the author—although both give the umbelliferon reaction with hydrochloric acid and ammonia. (See above, detection of galbanum or African ammoniacum in Persian ammoniacum.)

Kremel found (usual method)—

	Per cent. Resin.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h (V.-Z. h.)
1. Persian ammoniacum . .	67.7	112	30.6	142.6
2. Do. do. . .	67.1	110	50.0	160.0
3. Do. do. . .	70.7	100	50.5	150.5
4. African do. . .	77.6	59.0	123.0	182.0
From extract.				

As stated in the introductory remarks, nearly all published values for ammoniacum have been obtained with extracts—the foregoing among them.

There being no difficulty in distinguishing between Persian and African ammoniacum, and between the latter

and galbanum, by analytical means, the various unreliable qualitative colour reactions are therefore superfluous.

E. Dieterich found—

From extract	<i>Crudum.</i>		<i>Depuratum.</i>	
	Acid value, d. (S.-Z. d.)	57·12–105·45	78·96–135·00	
	Ester value (E.-Z.)	64·40– 91·22	73·00– 98·00	
	Sapon. value, h. (V.-Z. h.)	146·16–196·67	180·00–233·00	
	Loss at 100° C.	3·8 – 12·20%	2·15%	
	Ash	0·9 – 10·08%	1·05– 2·75%	

Solubility in—

Alcohol (96 per cent.), soluble	46·0 – 88·20%	66·50–76·53%
Do. do. insoluble	22·23– 42·96%	—

The acid, ester, and saponification values were determined by the same method as used by Kremel.

Beckurts and Brüche found—

No.	Commercial Variety.	Sp. gr. at 15° C.	Ash per cent.	Soluble in Alcohol per cent.	Acid Value, d. (S.-Z. d.).	Ester Value (E.-Z.).	Sapon. Value, h. (V.-Z. h.).
1	Depuratum	1·214	4·47	59	69	37	106
2	Do.	1·198	3·20	63	75	22	97
3	Do.	1·190	0·79	68	80	19	99
4	Do.	1·200	3·97	61	76	38	114
5	In granis	1·200	3·84	56	70	35	105
From extract.							

The author has worked out a new method for examining ammoniacum, in which the crude product is used and not an extract; and the results obtained therewith give the first values actually referring to the unaltered crude product. The acid value is determined in one of two ways, either by the Reichert-Meissl method—distilling off the volatile matter—or by dissociating the ammoniacum, adding alkali, and titrating back in exactly five minutes. Direct titration is impracticable owing to the absence of a well-defined colour-change, the end

point being masked by intermediate gradations of yellowish red. The operation of dissociating the crude drug with water and alcohol is necessary to dissolve out the acid constituents and render them accessible to the excess of alkali, which is left to act for only five minutes, since longer exposure would result in saponification. The total saponification value (G.-V.-Z.) is found, together with the resin (H.-Z.) and gum (G.-Z.) values by fractionation methods.

The *modus operandi* is as follows:—

(a) *Volatile acid value* (S.-Z. f.).¹—One-half gram. of ammoniacum is suffused with a little water in a flask through which a current of hot steam is then passed, the flask being placed in a heated sand bath to prevent excessive condensation of the steam. The receiver is charged with 40 c.c. of aqueous $\frac{n}{2}$ caustic potash, into which dips the tube coming from the condenser. Exactly 500 c.c. are distilled over, the tube is well rinsed with distilled water, from the top downwards, and the liquid is titrated back in presence of phenolphthalein. The number of c.c. of KHO combined gives the volatile acid value when multiplied by 28.08.

“In this case, the volatile acid value expresses the number of mgrms. of KHO which 500 c.c. of distillate, obtained from 0.5 gram. of ammoniacum by steam distillation, are capable of combining.”

(b) *Acid value, ind.* (S.-Z. ind.).—About one gram. of ammoniacum is boiled with 50 grms. of water for fifteen minutes, followed by 100 grms. of alcohol for an equal time, under a reflux condenser. After cooling, the weight is made up to 150 grms., and, after filtration, 75 grms. of filtrate (= 0.5 gram. of substance) are treated with 10 c.c. of alcoholic $\frac{n}{2}$ potash, left to stand for *exactly* five minutes,

¹ Säure Zahl flüchtig.

and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of KHO combined, multiplied by 28.08 and referred to 1 grm. of substance, gives the acid value (indirect).

(c) *Resin value and gum value* (H.-Z. and G.-Z.).—Two samples (1 grm. each) of ammoniacum are titrated, and each is suffused with 50 c.c. of petroleum benzine (sp. gr. 0.700 at 15° C.), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, and then left for twenty-four hours, at room temperature, in stoppered litre flasks, with frequent shaking. The one sample is then treated with 500 c.c. of water, and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein—this gives the “resin value.” The second sample is treated with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and left, with frequent shakings, for another twenty-four hours, to be then diluted with 500 c.c. of water, and titrated with $\frac{n}{2}$ sulphuric acid and phenolphthalein, accompanied by agitation. The result gives the “total saponification value” (G.-V.-Z.).

The respective quantities (c.c.) of KHO consumed multiplied by 28.08 give the corresponding values.

The “gum value” is found by subtracting the resin value from the total saponification value.

(d) *Loss at 100° C.*—Two grms. of ammoniacum are dried in the oven at 100° C. until constant.

All values must be calculated to the unaltered crude drug.

(e) *Test for galbanum.*—Five grms. of the finely ground ammoniacum are boiled in a small basin with 15 grms. of strong hydrochloric acid (sp. gr. 1.19) for fifteen minutes and filtered through a previously moistened, doubled filter. The clear filtrate is then carefully supersaturated with ammonia; whereupon, if galbanum be present, the liquid will exhibit, in reflected light, the characteristic blue fluorescence of umbelliferon.

The commercial varieties examined by the author gave the following results:—

Volatile acid value (S.-Z. f.) . . .	100-200
Acid value, ind. (S.-Z. ind.) . . .	90-105
Resin value (H.-Z.)	99·4 -155·4
Gum value (G.-Z.)	7·0 - 46·2
Total saponification value (G.-V.-Z.) .	145·6 -162·4
Loss at 100° C.	2·15-12 per cent.
Ash	not over 10 „

The author has also applied the method to adulterated samples, and found that in presence of adulterants the resin and total saponification values are diminished, as follows:—

Ammoniacum with—	Resin Val. (H.-Z.).	Gum. Val. (G.-V.).	Total Sapon. Val. (G.-V.-Z.).
5 per cent. of Galbanum .	112·00	15·4	127·40
10 „ „ .	124·60	5·2	129·80
20 „ „ .	120·40	15·4	135·80

So far as the acid value is concerned, that of the volatile matters is unsuitable for detecting adulteration; moreover, the method is a tedious one, and, like the Reichert-Meissl value method for fats, requires a deal of practice. On this account the author recommends the indirect acid value method as being more convenient and easier. It should be stated that a good ammoniacum ought to show a high volatile acid value and resin value, but a low gum value.

The following values were furnished by African ammoniacum examined by the author's method:—

Acid value, ind. (S.-Z. ind.) . . .	47·59- 92·21
Resin value (H.-Z.)	103·89-104·59
Total saponification value (G.-V.-Z.) .	105·30-108·10

The acid value (direct) in particular, of the African variety, fluctuates within rather wide limits, owing to the relatively considerable impurity of the drug. All the values are, in general, far lower than those given by Persian ammoniacum.

cum, and both the resin and the total saponification values are lower than in the case of galbanum (*q.v.*). A specimen of "ammoniacum depuratum" gave the acid value(ind.) 82·34-100.

Speaking generally, the author's method enables the crude drug to be used for analysis—bearing in mind the provisions laid down in the introductory remarks to this section—and also facilitates the accurate observation of the end-point in titration.

Mauch found that, like nearly all gum resins, ammoniacum is soluble in 60 per cent. chloral hydrate solution; and he recommends, for determining the gum, that the solution prepared with chloral hydrate (1-2 grms. in 10-15 grms.) should be filtered into 100 grms. of strong alcohol. By this means he obtained up to 21 per cent. of nearly pure gum.

Gregor and Bamberger found—

	Gregor.	Bamberger.
Methoxyl value (M.-Z.)	8·6	11·0
	9·0	—

(For the worth of these tests, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharm. tests for ammoniacum, see *Ph. C.*, 1898, No. 21.)

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43. Bdellium.

Gummi-resina Bdellium.

Origin and Habitat.—African bdellium: *Commiphora Africana*¹ (Burseraceæ); East Indian bdellium: *Balsamodendron Indicum* (Burseraceæ). Senegal, East Indies.

¹ The real origin of bdellium is just as uncertain as that of myrrh. See Holmes' *Ph. Ztg.*, 1899, No. 28, p. 237, and P. Siedler, *Ap. Ztg.*, 1897, No. 2.

Chemical Constituents.—Owing, as stated by Flückiger, to the circumstance that the experiments have been performed on specimens of doubtful origin—whether African or Indian—the constituents cannot be given with certainty. Flückiger found—resin, 70 per cent.; small quantities of ethereal oil and gum, 29 per cent.

General Properties and Commercial Varieties.—*East Indian bdellium* takes the form of shapeless agglomerated lumps about one inch in diameter, extremely dirty, resembling myrrh, and very impure. Externally they are rough, uneven, dull, and of dark brown colour, with a lustrous fracture, a sharp, bitter flavour, and an odour resembling Bisabol myrrh. With water the gum resin furnishes a whitish emulsion.

African bdellium is in reddish, oval or round lumps about half an inch across, which have a greasy lustre, and become soft and plastic when warmed. The gum resin gives with alcohol a golden yellow tincture, which is rendered turbid by water. Whereas a strip soaked in myrrh tincture and dried gives a bluish red coloration with nitric acid, this reaction does not occur in the case of bdellium (Berg).

As mentioned under Myrrh, bdellium does not give the reaction with bromine vapour, and it differs analytically from both varieties of myrrh (see below.) With regard to the origin and varieties of bdellium, Thiselton Dyer stated that this drug is exported from Berbera, a small port on the east coast of Africa, and is generally identified with the West African product on which the same name was bestowed by Guibourt. According to Royle, bdellium comes from *Balsamodendron Africanum*, Arnott, and Guibourt is of the same opinion; descriptions are given by Dymock and Parker. Royle's *Materia Medica* gives the report, communicated by Johnston in dealing with myrrh, that two varieties of the parent plant occur at Adel: the one, a low, thorny, ragged-

looking tree, described by Ehrenberg, yields the best commercial myrrh (*Balsamodendron myrrha*, or one of the forms of *B. opobalsamum*); the other, a tree rich in foliage, with coarsely serrated, dark green leaves, springing in fours or fives from a common centre, and with dried-up fruit berries, is probably *B. Kua*. Thiselton Dyer is of opinion that *B. myrrha* furnishes myrrh, and *B. Kua*, African bdellium.

Opaque bdellium is described by Parker as opaque, ochreous yellow in colour, with a conchoid fracture, very hard, inodorous, of bitter flavour, and often occurring as large, elliptical lumps with a granulated surface. It is shipped to India *viâ* Berbera. According to Dymock, opaque bdellium is often found in the bales of myrrh when these are sorted at Bombay; the drug is called "Meena harma," and is used as a remedy for the Guinea worm. According to the same author, opaque bdellium is of a yellowish white colour, similar to ammoniacum. Parker, however, regards Dymock's drug as the same gum resin that Vaughan names "Hotai." He states that the tincture from pure opaque bdellium gives an intense greenish black reaction with ferric chloride, whereas the Hotai tincture does not. Parker gives *Balsamodendron Playfairii* as the origin of bdellium.

Dymock, in his Indian Pharmacognosis, describes two kinds of Indian bdellium. The one, from *Balsamodendron Mukul*, resembles the African drug in general, but is lighter, and often greenish in colour, with different odour and taste; many of the lumps are vermiform in shape, and as thick as the little finger. This kind is worth about one-third less than the African drug. The second kind comes from *B. Roxburghii*, and is in irregular lumps, more or less covered with dirt, bark, and hair; it is of a greenish yellow colour, with a tinge of red. The consistence is waxy, soft, and brittle, the

odour peculiarly balsamic, recalling cedar wood, and the taste bitter. With water this grade forms a greenish white emulsion. It is not impossible that the two kinds are identical, and both derived from *B. Mukul*.

As even now, the published reports on the parent plants of myrrh, bdellium, and allied resins are still contradictory, any definite statement as to bdellium would be premature.

Adulterants.—Inorganic and vegetable impurities.

Analysis.—As already mentioned under Myrrh, the author has found bdellium give very low values in comparison with myrrhs; and it does not give the bromine reaction like Herabol myrrh.

Hirschsohn examined a number of specimens, and found the following percentages of solubility in petroleum ether:—

		Dried at 17° C.	at 120° C.	} Per cent. soluble.
Bdellium	Indicum . . .	13·37	11·29	
Do.	do.	16·57	9·87	
Do.	Africana . . .	36·09	35·61	
Do.	do.	35·68	34·79	
Do.	do.	21·70	20·31	

According to these figures, petroleum ether dissolves out considerably more from the African kinds than from the Indian. (See also the analytical differences below.)

Kremel found—

		74·3 per cent. of resin.	
From extract	{ Acid value, d. (S.-Z. d.)	28·3
	{ Ester value (E.-Z.)	119·3
	{ Saponification value, h. (V.-Z. h.)	147·6

the last three values by the usual method.

Bdellium being a myrrh-like gum resin, the author has examined it by precisely the same method as devised by himself for myrrh, and using the crude product instead of an extract, as follows:—

(a) *Acid value, d.* (S.-Z. d.).—One grm. of finely pulverised bdellium is taken from a large average sample of the powdered drug and suffused with 30 c.c. of distilled water, the whole being then heated for fifteen minutes under a reflux condenser. After adding 50 c.c. of strong alcohol, the mixture is boiled for fifteen minutes on a steam bath and under a reflux condenser. When cold, the liquid is titrated with alcoholic $\frac{n}{2}$ caustic potash and phenolphthalein until actual red coloration occurs. The $\frac{n}{2}$ alkali is used instead of $\frac{n}{10}$, because the colour-change is quicker and more sharply defined with a single drop of the stronger alkali than with the other. The acid value is found by multiplying the number of c.c. of consumed alkali by 28·08.

(b) *Saponification value, h.* (V.-Z. h.).—A second average sample (1 grm.) of bdellium is suffused with 30 c.c. of water, left to stand half an hour, and then treated with 25 c.c. of alcoholic $\frac{n}{2}$ potash. After boiling half an hour on the steam bath and under a reflux condenser—

(c) *The ester value* is obtained by subtracting the acid value from the saponification value.

(d) *Percentage soluble in alcohol.*—Ten grms. of substance are extracted with strong (96 per cent.) alcohol, and the extract is dried at 100° C. until constant.

The author has obtained the subjoined results :—

				Acid	Ester	Sapon.
				Value, d.	Value	Value, h.
				(S.-Z. d.).	(E.-Z.).	(V.-Z. h.).
African bdellium	.	.	.	∫ 12·79	70·00	82·79
				∖ 14·43	69·33	83·76
Do. do.	.	.	.	∫ 9·73	96·39	106·12
				∖ 11·96	95·57	107·53
Do. do.	.	.	.	∫ 19·21	90·66	109·87
				∖ 20·81	90·14	110·95
Indian do.	.	.	.	∫ 35·69	46·75	82·44
				∖ 37·19	48·46	85·65

These values are just as suitable for differentiating the two kinds, as the percentage of solubility in the petroleum ether method already mentioned.

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44. Euphorbium.

Gummi-resina Euphorbium (official in Germ. Pharm. III.).

Origin and Habitat.—*Euphorbia resinifera* (Euphorbiaceæ). Morocco.

Other species of *Euphorbia*, such as *E. Cattimandoo*, *E. evecorpus*, *E. pilulifera*, *E. helioscopia*, *E. geniculata*, *E. lathyris*, *E. Tirucalli*, also yield milky juices which contain euphorbon, are similar to euphorbium, and for the most part are utilised.

G. Henkel (*A. d. Ph.* 224, p. 729) examined numerous kinds of euphorbium, and his valuable work is worthy of special reference. He examined the drug from *E. resinifera*; *E. tetragona*; *E. Myrsinites*, L.; *E. orientalis*, L.; *E. virgata*, W.; *E. Lagasceæ*, Spr.; *E. humifusa*, W.; *E. splendens*, B.; *E. Canariensis*; *E. friogona*; *E. nereifolia*; *E. virosa*; *E. palustris*; *E. Gerardiana*; *E. verrucosa*, L.; *E. exigua*, L.; *E. Cyparissias*, L.

Chemical Constituents.—Euphorbon ($C_{15}H_{24}O$), 22 per cent.; gum, 18 per cent.; caoutchouc; salts of malic acid; ash, 10 per cent.; amorphous acrid resin, 38 per cent. (Flückiger.)

Pure euphorbium, divested of impurities, contains—euphorbon, 34.60 per cent.; resin soluble in ether, 26.95 per cent.; resin insoluble in ether, 14.25 per cent.; caoutchouc, 1.10 per cent.; malic acid, 1.50 per cent.; gum and salts, precipitable by alcohol, 8.10 per cent.; gum and salts, not thrown down by alcohol, 12.30 per cent.;

salts and organic matters soluble in ammonia, 1·20 per cent. (Henkel.)

Euphorbium, from *E. Cattimandoo*, exhibits similar constituents to that from *E. resinifera*—

Euphorbon, 35 per cent.; resin soluble in ether, 27·4 per cent.; resin insoluble in ether, 13·7 per cent.; caoutchouc, 1·5 per cent.; malic acid, 1·15 per cent.; gum and salts, precipitable by alcohol, 7·6 per cent.; gum and salts, not precipitable by alcohol, 12·15 per cent.; salts and organic matters, soluble in ammonia, 1·5 per cent. (Henkel.)

General Properties and Commercial Varieties.—

Readily pulverable, dull yellow lumps, enveloping the diacanthine leaf pads, the flower forks, and the three-lobed fruit. Euphorbium is slightly soluble in water, and almost completely so in alcohol. The taste is burning and acrid, and the powder induces sneezing.

Adulterants.—Inorganic and vegetable impurities.

Analysis.—Hirschsohn describes a kind of euphorbium, from *E. resinifera*, which yielded 20 per cent. of matters soluble in petroleum ether (drying effected at 120° C.). Euphorbium from *E. Tirucalli* gave 66·71 per cent.

According to Hirschsohn, this gum resin differs from ordinary euphorbium in being almost completely soluble in chloroform.

For the other kinds of euphorbium and their properties, see *A. d. Ph.* 224, pp. 729 *et seq.* (Henkel.)

Beckurts and Brüche found (usual method)—

		I.	II.	III.
From extract	{ Acid value, d. (S.-Z. d.) . . .	18	25	21
	{ Ester value (E.-Z.) . . .	63	68	49
	{ Saponification value, h. (V.-Z. h.)	81	93	70
	Ash	2·0%	1·8%	1·3%

but regarded the results as obtained from an insufficient

number of specimens to permit of any conclusions being drawn therefrom.

Kremel found—

Acid value, d. (S.-Z. d.)	13·4
Ester value (E.-Z.)	64·6
Saponification value, h. (V.-Z. h.)	78·0

by the usual method.

The author has devised the following method, based on the employment of the crude product instead of extracts, the saponification being effected by the fractional cold process, as in the case of other gum resins—

(a) *Acid value, d. (S.-Z. d.).*—About one grm. of finely pulverised euphorbium is suffused with 100 c.c. of alcohol, warmed for fifteen minutes under a reflux condenser, and titrated, when cold, with alcoholic $\frac{n}{2}$ potash and phenolphthalein until the red colour-change appears. The number of c.c. consumed, referred to 1 grm. of substance, gives the acid value.

(b) *Resin and total saponification value (H.-Z. and G.-V.-Z.).*—Duplicate 1 grm. samples are pulverised and suffused, each with 50 c.c. of petroleum benzine (sp. gr. at 15° C. = 0·700) followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, the whole being then left in stoppered litre flasks for twenty-four hours at room temperature, with frequent shaking. The one sample is then diluted with 500 c.c. of water, and titrated back by agitating with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the result giving the resin value. The second sample is treated further by adding 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 c.c. of water, and leaving for a further twenty-four hours, with frequent shaking. After dilution with 500 c.c. of water, the whole is titrated back by agitation with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the result giving the total saponification value.

The respective volumes (c.c.) of KHO consumed multiplied by 28·08 give the corresponding values. The difference between the two is the "gum value."

The following values were obtained by the author:—

	Acid Val., d. (S.-Z. d.).	Resin Val. (H.-Z.).	Total Sapon. Val. (G.-V.-Z.).	Gum Val. (G.-Z.).
1. Euphorbium electum .	13·4	{ 71·40 71·40	85·40 88·20	14·00 16·80
2. Do. pulvis .	25·0	{ 77·00 72·80	86·80 85·40	9·80 12·60
3. Do. do. .	21·00	{ 72·10 72·80	82·60 85·40	10·50 12·60
4. Do. do. .	19·60	{ 77·00 78·40	89·60 91·00	12·60 12·60

Gregor and Bamberger found—

	Methoxyl Value—	
	I.	II.
Gregor	0·0	2·8
Bamberger	0·0	0·0

(For the worth of these determinations, see *Chem. Rev.*, 1898, No. 10.) True analytical data for the scarcer varieties of euphorbium are altogether lacking.

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45. Galbanum.

Gummi-resina Galbanum (officinal in Germ. Pharm. III.).

Origin and Habitat.—*Peucedanum* (*Ferula*) *galbanifluum* and allied species (Umbelliferae). Persia.

Chemical Constituents.—Ethereal oil, 9·5 per cent., containing $C_{10}H_{16}$ and $C_{15}H_{24}$ (Wallace and Brühl), and oil ester (Conrady); resin soluble in alcohol, 63·5 per cent.; gum and impurities, 27 per cent. The pure resin contains

combined umbelliferon, 20 per cent.; galbaresinotannol ($C_6H_{10}O$ or $C_{18}H_{29}O_2OH$), and free umbelliferon, 0.25 per cent. According to Conrady, the galbaresinotannol and umbelliferon are present as umbelliferon galbaresinotannol ester.

General Properties and Commercial Varieties.—Agglomerated tears or masses, of wavy lustre and yellow or greenish colour. The *in massa* kind is impure, but contains much ethereal oil, to which its greasy consistence is due. The presence of the oil renders this kind particularly suitable for pharmaceutical purposes. The *in lacrymis* variety is purer, and in the form of grey globular masses which exhibit a white fracture. The drug always contains vegetable fragments. The odour is strongly balsamic, the flavour bitter, sharp, and burning. Galbanum is but partially soluble in water, alcohol, and other solvents. When boiled with hydrochloric acid and supersaturated with ammonia, the filtrate exhibits the beautiful blue fluorescence of umbelliferon. According to Holmes, the so-called fluid Persian galbanum comes from a species allied to *Peucedanum galbanifluum*, and is to be met with in commerce at the present time; the consistence is about that of turpentine. The difference that formerly existed between Levantine galbanum (in tears and mass) and Persian galbanum (in mass and as a viscous fluid) can now be scarcely maintained; similar gum resins being furnished by different species of *Ferula*, and Persia being the main source of the supply. According to Holmes, all galbanum is Persian, even though the produce of different species; consequently the differences stated by Hirschsohn to exist between the Persian and Levantine gum resins appear dubious. Thoms has recently proposed Laretia resin, from *Laretia acaulis* (Umbelliferae), which occurs in Chili, as a

substitute for galbanum. The resin contains umbelliferon, and gives, in a slight degree, the hydrochloric acid reaction prescribed for galbanum in the German Pharmacopœia, though not the ammonia reaction.

Adulterants.—Inferior extracted galbanum, sand, fatty oils, Persian and African ammoniacum, turpentine.

Analysis.—Apart from the odour, galbanum is distinguishable from ammoniacum by the presence of umbelliferon, and its reaction, and differs in appearance from African ammoniacum, which also gives the umbelliferon reaction.

Hirschsohn examined several kinds of galbanum, and gave chemical methods of distinguishing between the Persian and Levantine gum resin; but, as already stated, these are no longer applicable. According to this authority, galbanum *in massis* should contain not less than 60 per cent. of matters soluble in petroleum ether (drying temperature, 120° C.). Like Holmes, he also ascribed the fluid Persian galbanum to a separate species of *Ferula* or *Peucedanum*.

Kremel found—

					I.	II.
From extract	Resin, per cent				74·3	74·2
	{ Acid value, d. (S.-Z. d.)				28·3	28·3
	{ Ester value (E.-Z.)				119·3	132·2
	{ Saponification value, h. (V.-Z. h.) . .				147·6	160·5

by the usual method.

E. Dieterich found—

		<i>G. crudum.</i>	<i>G. depuratum.</i>
From extract	{ Acid value, d. (S.-Z. d.)	5·16– 68·80	19·32– 46·26
	{ Ester value (E.-Z.)	82·10–179·00	55·70– 91·40
	{ Sapon. value, h. (V.-Z. h.)	108·00–241·00	75·02–121·80
	Loss at 100° C. . . .	1·10– 30·98%	8·61%
	Ash	0·45– 31·31%	0·15– 2·10%
	Soluble in 90% alcohol . .	17·83– 71·50%	45·60–92·16%
	Insoluble in 90% alcohol .	45·58– 91·33%	11·40–37·24%
Water		21·40%	—

This authority was in favour of purifying the gum resin, since the percentage of ash would be thereby reduced by about one-half. (See Introductory Remarks to this section.)

Conrady, who occupied himself assiduously with galbanum, and must be regarded as a true connoisseur, states as follows:—

“My observations on the ash content, etc., fully coincide with the reports of E. Dieterich. So far as concerns the lower acid and ester values of galbanum this is readily explicable, in that, according to a private communication, the ethereal oil is first driven over with steam, and with it the free fatty acids, since, in view of the difficult saponification of galbanum, the liquid esters which are saponified by this treatment can alone be in question. The distillation could of course be easily dispensed with, and cold extraction with petroleum ether be practised, the unsaponified oil being then returned to the purified resin. In such case the *Galbanum depuratum* would really merit that title, and meet all the requirements of the Pharmacopœia; for I was able to detect both the free umbelliferon and also that combined by saponification. The purified galbanum also gives the same hydrochloric acid reaction as the crude drug, on which account a portion of the oil is probably not fully saponified.

“The sinking of the ester value is the sole noticeable difference from crude galbanum, and therefore a minimum ester value of 130 might be required of all galbanum. Of course, as already laid down by Lüdy for benzoin, an exact limit of time for the saponification process must be fixed. It would be still better, in the case of galbanum, to saponify 10·0 by the aid of steam, and titrate the distillate direct; this would mean that only the acid from the liquid esters would be titrated—the advantage of this being to facilitate the fixing of a standard for the acid and ester values within

narrow limits, owing to the slight fluctuation in the percentage of ethereal oil exhibited by the current commercial varieties of the drug."

Subsequently it was shown by the author that the determination of the acid value, as advocated by Conrady, cannot be effected so simply, but requires special precautions. Furthermore, the author has shown that his method of determining the acid value, based on the Reichert-Meissl principle, is tedious, and requires much practice. On this point more will be said later.

Beckurts and Brüche found—

	Sp. gr. at 15° C.	Ash %	Sol. in Alcohol %	From extract		
				Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).
1. G. depuratum	1.110	4.0	63	22	82	104
2. Do.	1.130	8.7	56	19	91	110
3. Do.	1.109	4.1	58	40	69	109
4. Do.	1.133	8.4	54	19	63	82
5. G. in granis	1.121	4.9	60	25	90	115

The authors remark that the ash content is in direct ratio to the sp. gr., so that galbanum with the highest sp. gr. also exhibits the largest percentage of ash. In addition, they recommend the acid, ester, and saponification values as means for detecting adulteration, without, however, giving any results obtained on this head.

The present author has worked out a new method for galbanum, and examined a large number of kinds, the results showing that Conrady's proposal for determining the acid value is impracticable; the exhibition of alkali being necessary to prevent loss.

As this method is nevertheless tedious, and entails much practice, the author applied to galbanum the same convenient method he uses for ammoniacum (*q.v.*), the gum resin being

dissociated, and then titrated back, for the same reasons as with ammoniacum. The resin, gum, and total saponification values are determined by the cold fractionation method. The author's method presents the advantages of furnishing liquids easily titrated, enabling the crude product to be used—not extracts—and giving concordant values, so far as these can *à priori* be expected from gum resins.

He proceeds as follows:—

(a) *Volatile acid value* (S.-Z. f.).—One-half gram. of galbanum, triturated as finely as possible, is suffused with a little water in a flask, through which hot steam is then passed, the flask being heated on a sand bath, in order to prevent excessive condensation. The receiver is charged with 40 c.c. of aqueous $\frac{n}{2}$ potash, into which dips the tube coming from the condenser. Exactly 500 c.c. are collected; the still tube is well rinsed with distilled water, from above downwards, and the liquid is titrated back in presence of phenolphthalein. The volatile acid value is calculated by multiplying the volume (c.c.) of consumed KHO by 28.08, and expresses the weight (mgrms.) of KHO fixed by 500 c.c. of distillate, obtained from 0.5 gram. of galbanum by steam distillation.

(b) *Acid value, ind.* (S.-Z. ind.).—About one gram. of galbanum is dissociated by boiling with 50 grms. of water and 100 grms. of alcohol in succession, each for fifteen minutes, under a reflux condenser. When cold, the weight is made up to 150 grms. with the employed substance, filtered, and 75 grms. of the filtrate = 0.5 gram. of substance are treated with 10 c.c. of alcoholic $\frac{n}{2}$ potash. After leaving for exactly five minutes the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the number of c.c. of KHO consumed multiplied by 28.08 and referred to 1 gram. giving the acid value.

(c) *Resin value (H.-Z.) and total saponification value (G.-V.-Z.).*—Two 1 grm. samples are each suffused with 50 c.c. of petroleum benzine (sp. gr. 0·700 at 15° C.), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, and left for twenty-four hours in closed 1 litre flasks, at room temperature, with frequent shaking. The one sample is then diluted with 500 c.c. of water, shaken up, and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the result giving the resin value. The other sample is treated further with another 25 c.c. of alcoholic $\frac{n}{2}$ potash and 75 c.c. of water, and left for another twenty-four hours, with frequent shaking. It is then diluted with 500 c.c. of water, and titrated back, by agitation, with $\frac{n}{2}$ sulphuric acid and phenolphthalein. This gives the total saponification value.

The respective volumes (c.c.) of KHO consumed give the corresponding values, after multiplication by 28·08. The difference gives the gum value.

(d) *Ash determination.*—One grm. of galbanum is incinerated carefully and calcined until found constant, after cooling in the desiccator.

(e) *Loss at 100° C.*—One grm. of galbanum is dried at 100° C. in the oven till constant.

The following limits of value were obtained by the author from a large number of specimens:—

Volatile acid value (S.-Z. f.)	. . .	73·5	–114·0
Acid value, ind. (S.-Z. ind.)	. . .	21·24	–63·45
Resin value (H.-Z.)	107·5	–122·5
Total saponification value (G.-V.-Z.)	116·2	–135·8
Gum value (G.-Z.)	8·4	–16·1
Ash	1–10 per cent.	
Loss at 100° C.	0·35	–31·5 „

Further analyses performed by the author show that, contrary to the opinion of Beckurts and Brüche, the ester,

and saponification values, or resin, total saponification, and gum values are not suitable for detecting adulteration, though the acid values are in both methods.

The results obtained are subjoined:—

Galbanum with—	Volatile Acid		Average.	Acid Value,
	Value			ind.
	(S.-Z. f.).			(S.-Z. ind.).
1. 5 % of ammoniacum .	75.60–	83.44	75.52	29.00–37.68
2. 10 % do. .	70.00–	79.52	74.67	33.00–47.00
3. 20 % do. .	59.92–	64.40	62.16	42.34–66.51
4. 5 % of asafœtida .	105.00–	117.60	111.30	34.77–46.13
5. 10 % do. .	119.28–	120.96	120.12	29.84–36.66
6. 20 % do.	{detectable by the odour, as were also 4 and 5. }			21.45–29.87

From these figures it is evident that adulteration with ammoniacum decreases the volatile acid value, whereas asafœtida has the reverse effect. Even as low as 5 per cent. of asafœtida is revealed by its penetrating smell during the distillation. On the other hand, the indirect acid value is raised by ammoniacum (which has a higher acid value), but is reduced by asafœtida.

Neglecting the qualitative reactions of Picards and Plugge, the quantitative acid values (*f.* and *ind.*) are to be recommended for this purpose.

The high percentage of ash—30 per cent.—is, of course, abnormal, 10 per cent. being the maximum that a good galbanum should exhibit—as expressed by the Swiss Pharmacopœia, which prescribes 8 per cent. of ash as the highest limit. No mention is made of ash content in the German Pharmacopœia.

Gregor and Bamberger found—

	Methoxyl value (M.-Z.).
Gregor	3.7
Bamberger	3.7

The worth of these values is criticised in *Chem. Rev.*, 1898, No. 10; and the Germ. Pharm. III. tests for galbanum in *Ph. C.*, 1898, No. 21. Finally, it may be mentioned that, according to Mauch, galbanum dissolves in 67 per cent. chloral hydrate, forming a yellow liquid, which is rendered milky by water and turbid by alcohol, gum being deposited. The umbelliferon reaction is also furnished by this solution.

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46. Gamboge.

Gummi-resina Gutti (officinal in Germ. Pharm. III.).

Origin and Habitat.—*Garcinia Morella*, D. (Clusiaceæ). Siam, Ceylon.

Chemical Constituents.—Gum (13·8 per cent.), resin, gambogic acid (70 per cent.), wax and ash, vegetable detritus; no ethereal oil.

General Properties and Commercial Varieties.—Gamboge comes on the market in the form of pipes, up to three inches thick; also cakes or lumps, of reddish yellow colour and large conchoid lustrous fracture. At 20° C. they float in carbon di-sulphide, but sink at higher temperatures; and they furnish a yellow emulsion with water. The mass is plastic at 100° C.; it is only partially soluble in water, alcohol, and ether, and the solution has an acid reaction. The pipe forms are the best, then the cakes, and lastly, the mass form. There are two chief commercial varieties—Siam gamboge and Ceylon gamboge, but the latter is rare.

Adulterants.—Vegetable impurities, rice meal, sand, dirt, starch, dextrin, and colophony; the last-named, in particular, being used to adulterate the powder.

Analysis.—Gamboge has been frequently analysed.

Williams found (usual method)—

Acid value, d. (S.-Z. d.)	80.6
Ester value (E.-Z.)	67.2
Saponification value, hot (V.-Z.-h.)	147.8
Ash	0.48 per cent.
Moisture	3.70 „

Costelo exhausted 10 grms. of various samples, with alcohol, and found—

	Resin.	Gum.	Impurities.	Total sol. in Alcohol.
Gamboge in { Lumps	6.76	2.74	0.38	9.88
{ Pipes	7.93	1.94	0.15	9.89
{ Powder	7.66	2.25	0.07	9.98

the balance being moisture.

Von Schmidt and Erban found solubility in—

Alcohol	} partly soluble.
Ether	
Methyl alcohol	
Amyl alcohol	
Benzol	
Petroleum ether	
Acetone	
Glacial acetic acid	
Chloroform	
Carbon di-sulphide	
Oil of turpentine	

From extract { Acid value, d. (S.-Z. d.)	80.3	} not examined.
{ Ester value (E.-Z.)		
{ Saponification value, h. (V.-Z. h.)		

The foregoing values, being obtained from extract, are of merely relative worth in forming an opinion.

A. Kremel found—

	Resin	79·6 per cent.
From extract	{ Acid value, d. (S.-Z. d.) . . .	100·0
	{ Ester value (E.-Z.)	56·7
	{ Saponification value, h. (V.-Z. h.) . . .	156·7

Kremel's figures also were obtained from extracts, and their value is therefore only relative.

Beckurts and Brüche found—

		I.	II.	III.	IV.
	Ash, per cent.	0·49	0·63	0·58	0·71
From extract	{ Acid value, d. (S.-Z. d.) . . .	89	81	69	71
	{ Ester value (E.-Z.)	61	50	43	44
	{ Saponification value, h. (V.-Z. h.)	150	131	112	115

The remarks made on Kremel's values also apply here.

As the best neutral solvent for gamboge the author recommends: strong alcohol, 2 parts; water, 1 part,—used in succession, not together. He has determined the acid value (direct), resin, total saponification, and gum values of the natural drug—not extract—(see fractional saponification in Part I.) by the following methods:—

(a) *Acid value, direct* (S.-Z. d.).—One gram. of the finely triturated natural gamboge is warmed with 100 grms. of alcohol under a reflux condenser for fifteen minutes, 50 grms. of water being added, and the whole left to stand until as much as possible has been dissolved. When quite cold, the liquid is titrated with alcoholic $\frac{n}{2}$ caustic potash until the added drops of alkali no longer turn red, but the whole liquid assumes a red coloration.

(b) *Resin value and total saponification value* (H.-Z. and G.-V.-Z.).—Two 1 gram. samples of finely triturated gamboge—taken as average samples of a larger quantity—are each suffused with 25 c.c. of alcoholic $\frac{n}{2}$ potash, and are left for

twenty-four hours in tightly stoppered flasks. The one sample is then diluted with water and titrated, the volume (c.c.) of KHO consumed multiplied by 28·08 giving the resin value. The second sample receives an addition of 25 c.c. of aqueous $\frac{n}{2}$ potash, and is titrated back after standing twenty-four hours longer, the result giving the total saponification value. The gum value is obtained by difference.

This method enables the natural drug to be used, and also furnishes a readily detectable colour-change at the end-point. The preliminary dissociation with alcohol and water, in the proportion of 2 to 1 for the acid value determination, gives an almost complete solution easily titrated.

The author obtained the following values :—

		Acid Value, d. (S.-Z. d.)—	
Natural gamboge (pipes)		1. 71·45	5. 86·46
		2. 78·60	6. 83·60
		3. 79·31	7. 84·31
		4. 85·03	
	Resin Val. (H.-Z.).	Total Sapon. Val. (G.-V.-Z.).	Gum. Val. (G.-Z.).
1. Gamboge, <i>naturale</i>	$\begin{cases} 109\cdot20 \\ 110\cdot60 \end{cases}$	$\begin{cases} 127\cdot40 \\ 131\cdot60 \end{cases}$	$\begin{cases} 18\cdot20 \\ 21\cdot00 \end{cases}$
2. Do. <i>pulvis</i>	$\begin{cases} 110\cdot60 \\ 112\cdot00 \end{cases}$	$\begin{cases} 124\cdot60 \\ 133\cdot00 \end{cases}$	$\begin{cases} 14\cdot00 \\ 21\cdot00 \end{cases}$
3. Do. <i>naturale</i>	$\begin{cases} 105\cdot00 \\ 107\cdot80 \end{cases}$	$\begin{cases} 121\cdot80 \\ 124\cdot60 \end{cases}$	$\begin{cases} 16\cdot80 \\ 16\cdot80 \end{cases}$
4. Do. <i>do.</i>	$\begin{cases} 110\cdot60 \\ 110\cdot60 \end{cases}$	$\begin{cases} 128\cdot80 \\ 128\cdot80 \end{cases}$	$\begin{cases} 18\cdot20 \\ 18\cdot20 \end{cases}$
5. Do. <i>electum</i>	$\begin{cases} 114\cdot80 \\ 116\cdot20 \end{cases}$	$\begin{cases} 137\cdot20 \\ 138\cdot60 \end{cases}$	$\begin{cases} 22\cdot40 \\ 22\cdot40 \end{cases}$

The “pulvis” variety seems, like nearly all resins in powder, to be adulterated with colophony.

A further noteworthy contribution on the testing of

gamboge is supplied by Eberhardt, who principally examines for starch.

He proceeds as follows:—

One grm. of the powder to be tested is dissolved in 5 c.c. of potash, followed by an addition of 45 c.c. of water, and finally an excess of hydrochloric acid. The turbid liquid is then filtered through cotton-wool, and one or two drops of iodine are added to the clear filtrate. In presence of over 2 per cent. of starch there immediately ensues a dark blue coloration, or a similarly coloured precipitate is formed. The powdered commercial drug usually gives a yellow coloration, which afterwards turns blue; pure gamboge, with 1 per cent. of added starch, gives a dull blue, which deepens on standing, and deposits a precipitate after several hours. Five to ten per cent. of starch gives a blue precipitate immediately. Five per cent. and under of turmeric gives decided starch reactions. If a precipitate be obtained at once, adulteration may be assumed, though sometimes adulterants are present when the drug is free from starch, in which event the resin determination is the best test. Eberhardt determined the resin content in several specimens free from starch by dissolving in alcohol, and found 75.9–81.4 per cent. soluble, with 18.6–24.1 per cent. of residue.

Woolsey also reports on adulterated gamboge, and lays down the minimum resin content as 70–80 per cent., with 3–4 per cent. as the maximum for ash, and 4–6 per cent. moisture.

According to Mauch, gamboge is soluble in five parts of a 60 per cent. solution of chloral hydrate. If the gum be determined by precipitation with alcohol, a very pure product (gum), amounting to 16 per cent., is obtained (Mauch). The method is also applicable to the detection of impurities (see *Asafoetida*).

Kitt determined the carbonyl value (C.-Z.) of gamboge as 1.25–1.38.

Gregor and Bamberger examined the methoxyl value, and found—

		Methoxyl Value (M.-Z.)—	
Gregor	3.7	0.0
Bamberger	3.7	0.0

(For the worth of these determinations, see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharmacopœia tests, see the author's remarks in *Ph. C.*, 1898, No. 21.)

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47. Lactucarium.

Lactucarium Germanicum.

Origin and Habitat.—*Lactuca virosa*, L. (Compositæ). Europe.

Chemical Constituents.—Lactucin (crystalline, bitter principle), $C_{11}H_{14}O$; lactucic acid (bitter and crystalline) (Kromayer); lactucon (neutral and crystalline), $C_{15}H_{24}O$ (Ludwig) or $C_{19}H_{30}O$ (O. Schmidt); asparagin (?); caoutchouc; ash, 10 per cent.; mannite (?). English lactucarium is of similar composition, there being no appreciable divergences.

General Properties and Commercial Varieties.—*Lactucarium Germanicum* forms tough, homogeneous, yellow-brown masses, somewhat waxy in fracture and hygroscopic. The taste is irritant, bitter, and narcotic. It is only partially soluble in water, ether, and alcohol.

Lactucarium Anglicum, which is also derived from *Lactuca virosa*, consists of irregular, larger and smaller granules, more or less obtuse angled, dull, friable, dark brown in colour, and non-hygroscopic.

Lactucarium Gallicum, the “Thridax” of the ancients, comes from *Lactuca sativa*, and forms a fatty extract, blackish brown in colour. A lactucarium is also furnished by *L. Canadensis*.

Adulterants.—Inferior vegetable extracts, and various kinds of bread.

Analysis.—No true analytical data on the German variety are available.

Hanausek reported on an imitation lactucarium, consisting of brown granules of various sizes, devoid of odour or flavour, and swelling up in water, to then fall into smaller granules. The examination showed the goods to consist of old wheaten bread.

Kremel found an admixture of bread crumbs in various specimens of lactucarium, the adulteration being detectable by both chemical and microscopical means. If lactucarium be treated in an extractor, with 3 parts of alcohol and 1 of chloroform, the lactucon is the chief constituent dissolved, the extract amounting from 55–69 per cent. in the case of the pure drug. When an admixture of bread is present, the percentage of extract is proportionally lower, and the percentages of moisture and ash are also affected thereby. The following analyses of three kinds of lactucarium may serve as examples :—

	Moisture	Ash	Chloroform-alcohol Extract
	%	%	%
I.	5.80	6.50	57.46
II.	5.88	4.51	40.00
III.	10.84	1.61	11.54

No. I. was pure *Lactucarium Germanicum*; Nos. II. and III., adulterated *L. Austriacum*. Swollen starch granules could be detected in the two latter under the microscope, and a blue coloration was furnished on testing a boiled sample with iodine, when cold.

According to Kremel, lactucarium yields at least 50 per cent. of matters soluble in a mixture of 3 parts of alcohol and 1 of chloroform.

The author has examined German and English lactucarium, and determined the resin and total saponification values by fractional saponification, according to the following method :—

Two 1 gram. samples of lactucarium are triturated, and each suffused with 50 c.c. of petroleum benzine (sp. gr. 0.700), followed by 25 c.c. of alcoholic $\frac{n}{2}$ potash, the whole being left to stand in the cold for twenty-four hours in stoppered litre flasks, with frequent shaking. The one sample is then diluted with 500 c.c. of water, and at once titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, by agitation, the results giving the resin value. The second sample is further treated with 25 c.c. of aqueous $\frac{n}{2}$ potash and 75 grms. of water, and is left for another twenty-four hours, with frequent shaking, at the end of which time it is diluted with 500 c.c. of water and titrated back by $\frac{n}{2}$ sulphuric acid and phenolphthalein, with agitation. The resulting figures represent the perfect "total saponification value." The gum value is ascertained by difference.

The author obtained the following values:—

				Resin Value (H.-Z.).	Total Sapon. Value (G.-V.-Z.).	Gum Value (G.-Z.).
1.	Lactucarium Germanicum	pulvis		{ 203·00 207·20	215·60 217·00	12·60 9·80
2.	Do.	do.	in massa	{ 154·00 156·80	166·60 169·40	12·60 12·60
3.	Do.	do.	pulvis	{ 189·00 191·80	191·80 191·80	2·80 0·00
4.	Do.	do.	do.	{ 249·20 252·00	310·80 313·60	61·60 61·60
5.	Do.			{ 163·80 162·40	190·40 184·80	26·60 22·40
6.	Do.	Anglicum		{ 68·60 67·20	75·60 75·60	7·00 8·40
7.	Do.	do.		{ 225·40 225·40	232·40 238·00	7·00 12·60
8.	Do.	do.		{ 50·40 51·80	75·60 78·40	25·20 26·60

Whereas the figures obtained with German lactucarium fluctuate within relatively narrow limits—when the two classes “pulvis” and “massa” are considered by themselves—those furnished by the English drug indicate very irregular composition. As in the case of nearly all resinous products, the “pulvis” varieties of German lactucarium gave the highest values, so that here also an adulteration with colophony may be assumed (see conclusion to Part I.).

(For the detection of colophony, by the Storch-Morawski reaction, see under Colophony.)

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48. Myrrh.

Gummi-resina Myrrha (*Herabol Myrrh* officinal in German Pharmacopœia III.).

I. HERABOL MYRRH (the usual commercial grade).

Origin and Habitat.¹—Species of *Balsamodendron* and *Commiphora* (Burseraceæ). Arabia.

Chemical Constituents.—Gum, 57–59 per cent.; resin; and ethereal oil. The first-named corresponds to the formula $C_6H_{10}O_5$. The portion readily soluble in alcohol is a mixture of various resins: a neutral resin, and a soft resin (soluble in alcohol) of the formula $C_{26}H_{34}O_5$, with three hydroxyl groups and two resin acids. One of the latter is dibasic, and has the formula $C_{13}H_{16}O_8$; the other, also dibasic, having the formula $C_{26}H_{32}O_9$. Ethereal oil, 7–8 per cent., the chief constituent of which has the formula $C_{10}H_{14}O$. (O. Köhler.)

General Properties.—Myrrh occurs in the form of masses or granules as large as a nut, yellowish red in colour, with a greasy, lustrous, fine-grained fracture, not smooth and conchoid. Water produces a white emulsion; alcohol dissolves only the resin. The odour is strong, and the taste persistently bitter and irritant. Herabol myrrh is the so-called “male myrrh.”

Adulterants.—Extracted myrrh resin, bdellium, gum arabic, Bisabol myrrh.

II. BISABOL MYRRH.

Origin and Habitat.—(See note to Herabol myrrh.) *Balsamea erythrea*, Engl. (Burseraceæ). Somaliland.

¹ In spite of numerous researches, the conflicting views published on the origin of myrrh, bdellium, and similar bodies have not yet been fully settled. Consequently, any definite statement would be premature. On this point, see Holmes, *Ph. Ztg.*, 1899, pp. 237–238, and P. Siedler, *Ap. Ztg.*, 1898, No. 2.

Chemical Constituents.—Gum soluble in water, 22.1 per cent.; gum soluble in caustic soda, 29.85 per cent.; crude resin, 21.5 per cent.; bitter principle, 1.5 per cent.; ethereal oil, 7.8 per cent.; water, 3.17 per cent.; vegetable detritus, 13.4 per cent. The ethereal oil contains a hydrocarbon, bisabolene, of the formula $C_{10}H_{16}$, as also ester-like compounds and an oxygenated body ($C_{56}H_{96}O$), corresponding to a doubled molecule of chironol ($C_{28}H_{48}O$), minus one atom of oxygen (see Opopanax). The pure resin contains free acids, a resene (Bisabol resene), and a neutral substance. (Tucholka.)

General Properties and Commercial Varieties.—Similar to Herabol myrrh, but with a milder and weaker taste and smell, more like bdellium. This Bisabol myrrh is known as "female myrrh."

Adulterants, etc.—Bisabol myrrh can only be confounded with Herabol myrrh. It is generally consumed in the producing countries, and is rarely met with in commerce.

Other kinds of myrrh, such as Arabian, Meetiya, Persian, and Chinaibol (Siam) myrrh, are of interest to the producing countries exclusively, and not to the European trade. Hooper recommends as an excellent substitute for myrrh, the gum resin from *Balsamodendron Berryi*, known as *Mulukilivary* in its East Indian home. This myrrh contains 84 per cent. of gum, 5 per cent. of water, and 6.6 per cent. of mineral matter. The gum is not precipitable by lead acetate, thus differing from the gum in ordinary myrrh; the soft resin is dextro-rotatory, and is soluble in ether, alcohol, chloroform, and carbon di-sulphide. A similar substitute for myrrh is "Bayee balsam," the gum resin furnished by *Balsamodendron pubescens*. The gum left behind in the production of the alcoholic preparations of myrrh is often utilised technically as an agglutinant.

Analysis.—The bromine reaction repeatedly advised—and indeed accepted in several Pharmacopœiæ—has been subsequently characterised as unreliable by an equal number of authorities.

If myrrh be extracted with alcohol, and the evaporation residue be taken up with ether, bromine vapour is said to give a red-violet colour reaction. Another reaction, also unreliable since it frequently fails, with old or powdered myrrh in particular, is that wherein the myrrh is brushed with alcohol and nitric acid, which treatment should give a local cloudy violet coloration. Herabol and Bisabol myrrh are so remarkably different analytically, that the above reaction—which is not given by Bisabol myrrh—is superfluous, the more so that Bisabol myrrh is at once distinguishable by its odour and appearance, and is, moreover, not met with in commerce at all. Tucholka gives the following reaction for distinguishing between Herabol and Bisabol myrrh:—

“Six drops of a petroleum-ether extract (1 : 15) are mixed with 3 c.c. of glacial acetic acid and floated on the surface of 3 c.c. of concentrated sulphuric acid. A beautiful rose red zone immediately forms at the surface of contact, and after a short time the coloration extends throughout the entire layer of acetic acid, and remains persistent. When a stronger extract is used, a brown coloration is produced. With this reagent the officinal myrrh gives only a very pale rose coloration to the acetic layer, and the colour does not increase in strength; the surface of contact between the two strata shows at first a green colour, which turns brown with green fluorescence on standing.”

Neither bdellium nor Bisabol myrrh gives the bromine vapour reaction furnished by Herabol myrrh; and bdellium can also be readily distinguished from both kinds of myrrh by analytical means (see below).

Hirschsohn examined numerous specimens, and prescribes that the extract in petroleum ether should be colourless, and not exceed 6 per cent. in amount on drying at $120^{\circ}\text{C}.$, a higher percentage indicating adulteration. The presence of sulphur in these residues is said to point to the presence of bdellium. (In the present state of our knowledge the presence of sulphur compounds of bdellium is dubious, so that it is not quite clear on what the above inference is based. Asafoetida or sagapenum—both of which contain sulphurous oils—would be more probable, were it not that adulteration with these substances is precluded as too remote.) The petroleum ether should be colourless after the extraction.

The Pharmacopœiæ mostly confine themselves to the bromine reaction, and the prescription of a 30 per cent. minimum for the soluble in alcohol, and 6–8 per cent. for the ash.

The author has found that the percentage soluble in alcohol is greater in Herabol myrrh (up to 50 per cent.) than in Bisabol myrrh (up to 20 per cent.).

Kremel found for Herabol myrrh—

		I.	II.	III.
From extract	Resin	39·5%	42·0%	23·9%
	Acid value, d. (S.-Z. d.) .	64·0	60·2	70·3
	Ester value (E.-Z.) .	95·0	116·5	145·8
	Sapon. value, h. (V.-Z. h.)	159·0	176·7	216·1

And for Indian myrrh—

From extract	Resin	30·7%
	Acid value, d. (S.-Z. d) .	42·1
	Ester value (E.-Z.) .	130·8
	Sapon. value, h. (V.-Z. h.) .	172·9

by the usual method.

E. Dieterich found solubility in—

Water	37·30–52·50 per cent.
Alcohol (96 per cent.)	22·6 per cent.

Tucholka used Kremel's method in his examination of Bisabol myrrh, and, as might have been expected, could not discover any analytical difference between the two kinds of myrrh. The present author examined the same Bisabol myrrh by his own method, and expressed himself on the subject as follows:—

“As in the case of many other resins and gum resins, the error of using an alcoholic extract—on which point I have already dilated in the *H. A.*, 1896, p. 126 sec. i.—has been committed. This is wrong, because, in the first place, alterations take place in the substance itself during the preparation of the extract, and—which is the main defect—an unknown and uncalculated loss of volatile matter occurs in the concentration of the extract, especially in the case of such gum resins, *e.g.* ammoniacum, galbanum, myrrh, etc., as contain ethereal oils and volatile constituents, the loss varying with the percentage present. The resulting fluctuations are the greater because no account is taken of the degree of solubility in alcohol on the one hand and the percentage of volatile matters on the other, the alcoholic extract being classed as the equivalent of the gum resin itself. When it is remembered that the percentage soluble in alcohol is only from 20 to 30 per cent. in the case of Bisabol myrrh, and is therefore equal to barely about one-third of the total weight of the drug, it can be readily estimated how far the results obtained are from corresponding to the entire drug, and what fluctuations the values must *eo ipso* undergo. In many instances, in place of using a quantity of extract corresponding to 1 grm. of the drug, the values have been determined in 1 grm. of extract; consequently, as this quantity corresponds to much more than 1 grm. of gum resin, the resulting values do not represent the number of mgrms. of KHO fixed by 1 grm. of drug, but

something else quite at variance with the true definition of the term 'acid value.'

"It is therefore not to be wondered at that, with reference to the acid and saponification values, Tucholka arrived at results which were unsatisfactory and did not afford any distinction between the two sorts of myrrh. The divergent and unreliable character of the values obtained, when extracts are used instead of the natural drug, may be gathered from the subjoined figures. Kremel found for Herabol myrrh, with extract, the acid value, $d. = 60.2-70.3$; ester value = $95.0-148.4$; and saponification value, $h. = 159-260.1$. The author obtained by the same method, from an extract equal to 20 per cent. of the drug, the acid value, $d. = 11.2$; ether value = 33.6 ; and saponification value, $h. = 44.8$. These enormous differences sufficiently show how inexact is the examination of extracts, and this is still more clearly evident by the differences found with Bisabol myrrh. Here Tucholka obtained from extract the acid value, $d. = 55.7$; ester value = 87.6 ; saponification value, $h. = 143.3$: whilst the author, using an extract equal to a 50 per cent. yield, found the acid value, $d. = 5.6$; ester value = 51.4 ; and saponification value, $h. = 57.00$.

"The values come out very different and much higher when the natural drug is taken for examination, the higher results clearly showing that large quantities of volatile matters are lost during the preparation of the extract, and that the residue insoluble in alcohol also contains acid- and ester-like constituents.

"On the basis of numerous experiments, I have now devised a method which enables the natural drug to be used, and both parts of the myrrh—the resin soluble in alcohol and the gum soluble in water—to be taken into account."

The method referred to is as follows:—

(a) *Acid value, d.* (S.-Z. d.)—One grm. of finely triturated myrrh, taken as an average sample, is suffused with 30 c.c. of distilled water and warmed for fifteen minutes under a reflux condenser. Fifty c.c. of strong alcohol are added, and the whole is boiled for another fifteen minutes in a steam bath and under a reflux condenser. After cooling down, the liquid is titrated with alcoholic $\frac{n}{2}$ potash and phenolphthalein until a true red coloration is produced. The strong alkali is used in preference to the decinormal, because it gives the end-point quicker and more clearly defined. The multiplication of the consumed volume (c.c.) of alkali by 28.08 gives the acid value.

(b) *Saponification value, h.* (V.-Z. h.)—A further 1 grm. average sample is suffused with 30 c.c. of water, left to stand half an hour, then treated with 25 c.c. of alcoholic $\frac{n}{2}$ potash and boiled for half an hour on the steam bath and under a reflux condenser. After cooling and diluting with alcohol it is titrated back, and the volume (c.c.) of KHO consumed multiplied by 28.08 gives the saponification value.

(c) *The ester value* is found by difference.

In addition, the percentage soluble in alcohol must be determined by extracting the drug with strong alcohol in a Soxhlet apparatus.

Although, in view of the varying percentage of ethereal constituents, the values furnished by this method are subject to a certain degree of fluctuation, they nevertheless correspond thoroughly to the original drug, especially when care is taken to obtain a true average sample.

The author obtained the following values:—

Myrrh.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).	Percent. sol. in Alcohol.
Bisabol myrrh .	20.06	125.54	145.60	50
Herabol do. .	25.48	204.12	229.60	20

A comparison of the figures obtained by the author with those found by Tucholka in examining extracts shows that this new method is the only one enabling the two kinds of myrrh to be distinguished, whereas both kinds exhibit about the same acid value, they differ considerably in the ester and saponification values—the commercial Herabol grade giving far higher figures than Bisabol myrrh.

This peculiarity, in despite of the fact that the percentage of Herabol myrrh soluble in alcohol does not exceed 20 per cent., indicates that the gummy matters soluble in water, that were left out of consideration in the old method, contain an almost greater amount of acid- and ester-like constituents than the alcoholic extract. Special recommendation can be given to the Tucholka qualitative method (see above) in addition to the aforesaid quantitative tests.

When the values given under bdellium are compared with those found for myrrh, it is seen that (East Indian and African) bdellium gives the lowest and Herabol myrrh the highest figures of these three allied gum resins, whilst Bisabol myrrh occupies a medium position.

About eight per cent. should be the highest permissible limit of ash content for officinal Herabol myrrh.

Gregor and Bamberger found the following methoxyl values (M.-Z.) :—

Gregor	13.5
Bamberger	13.2-13.6

(For the worth of these determinations, see *Chem. Rev.*, 1898, No. 10.)

Mauch estimated the gum in Herabol myrrh by dissolving 1–2 grms. of the gum resin in 10–15 grms. of 60 per cent. chloral hydrate, and weighing the gum thrown down by 100 grms. of strong alcohol. He found 75.2 per cent. of gum. According to the same authority, this myrrh dissolves to a clear yellow-brown liquid in 8–10 parts of 60 per cent. chloral hydrate.

(On the Germ. Pharm. III. tests for myrrh, see *Ph. C.*, 1898, No. 21.)

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49. Opopanax.

Gummi-resina Opopanax.

Origin and Habitat.—There are two distinct varieties—I. *Burseracea opopanax*, from *Balsamodendron Kafal* (Knuth), Persia; and II. *Umbellifer opopanax*, from *Chironium opopanax* (Koch), Southern Europe.

Other species of *Commiphora* yield gum resins similar to opopanax. The *Burseracea* variety is the kind now in commercial use for perfumery.

I. BURSERACEA OPOPANAX.

Chemical Constituents.—Ethereal oil, 6.5 per cent.; gum and vegetable detritus, 70 per cent.; moisture and loss at 100° C., 4.5 per cent.; resin, 19 per cent. The resin consists of— α -panaxresene ($C_{32}H_{54}O_4$); β -panaxresene ($C_{32}H_{52}O_5$), panaxresinotannol ($C_{34}H_{50}O_8$), an alcohol, chironol ($C_{28}H_{48}O$) (a new type), and bitter principle (Baur).

II. UMBELLIFER OPOPANAX.

Chemical Constituents.—Resin soluble in ether, the ferulaic ester of oporesinotannol, 51.80 per cent.; resin insoluble in ether, free oporesinotannol ($C_{12}H_{13}O_2OH$), 1.9 per cent.; gum (a mixture of the approximate formula $C_8H_{14}O_7$), 33.782 per cent.; ethereal oil, with the oponal ($C_{20}H_{10}O_7$) isolated therefrom, 8.3 per cent.; free ferulaic acid ($C_{10}H_{10}O_4$), 0.216 per cent.; vanillin, 0.00272 per cent.; moisture, 2 per cent.; bassorin and vegetable detritus, 2 per cent.; and bitter principle (Knihl).

General Properties and Commercial Varieties.—Burseracea opopanax, which at the present time is about the only variety found in commerce, forms large, brown-yellow lumps, interspersed with paler gummy granules, together with smaller perfectly white lumps. The odour is peculiar, somewhat recalling Sumbul and Bisabol myrrh; and some kinds have a wonderfully fine odour, which at once indicates their value for perfumery purposes.

The perfume sold as “opopanax” is said to have nothing to do with the gum resin, but is, according to Holmes, the ethereal oil from *Commiphora Kataf*.

The name “myrrh” has been bestowed on the gum resin by transition from the perfume (coming as this does from a *Commiphora* allied to myrrh), although the gum resin itself, especially the Umbellifer opopanax, has nothing to do with true myrrh.

Umbellifer opopanax when fresh is in greasy masses or brownish yellow lumps, smelling something like levisticum or galbanum—at anyrate, strong and disagreeable—and with a strongly bitter balsamic taste.

Adulterants and Admixtures.—The two kinds, one for the other; also myrrh, bdellium, and galbanum.

Analysis.—Hirschsohn examined several varieties of opopanax, but with such discordant results that the data will not be repeated here.

The author has only recently published sundry analytical particulars of Burseracea and Umbellifer opopanax. As in the case of myrrh, he worked with the natural product, instead of extracts, and proceeded in the following manner:—

(a) *Acid value, d.* (S.-Z. d.).—One grm. of the finely triturated opopanax, taken as an average sample from a larger quantity, is suffused with 30 c.c. of distilled water and warmed for fifteen minutes under a reflux condenser, 50 c.c. of strong alcohol being then added and the whole heated to boiling for another fifteen minutes in the steam bath and still under a reflux condenser. When the liquid has cooled down, it is titrated with alcoholic $\frac{n}{2}$ potash until a true red coloration is produced. The stronger alkali is used in preference to the decinormal, because of the sharper and quicker end reaction it produces. The acid value is found by multiplying the volume (c.c.) of consumed KHO by 28·08.

(b) *Saponification value, h.* (V.-Z. h.).—A further 1 grm. average sample is suffused with 30 c.c. of water, left to stand half an hour, and then treated with 25 c.c. of alcoholic $\frac{n}{2}$ potash. After boiling for half an hour in the steam bath and under a reflux condenser, and leaving to cool down, the liquid is diluted with alcohol and titrated back. The number of c.c. of combined KHO multiplied by 28·08 gives the saponification value.

(c) The *ester value* (E.-Z.) is found by difference.

He found the following values:—

Burseracea Opopanax.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).
1.	23·84 30·92	83·01 97·24	105·85 128·16
2.	10·46 16·40	85·74 81·94	96·20 98·34
3.	24·03 28·20	125·01 124·62	149·04 152·82

The following specimens of Umbellifer opopanax were, in part, obtained direct from Teheran:—

Umbellifer Opopanax.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).
1. Liquid Teheran opopanax (Jovishir drops)	f 32·43 l 33·06	105·46 119·58	137·89 152·64
2. Solid Teheran opopanax (Jovishir dry)	f 35·00 l 36·86	114·07 126·90	149·07 163·76
3. Solid opopanax (old)	f 53·40 l 58·57	142·60 140·50	196·00 199·07

The above method is allied to those used for myrrh, bdellium, and sagapenum, but differs considerably from those employed for ammoniacum and galbanum, because the latter are saponified by the cold, or fractionated, method, whilst the former are saponifiable by the hot process alone. As in the case of galbanum and ammoniacum, a preliminary dissociation of the gum resin is here indispensable. It will be seen from the foregoing tables that Umbellifer opopanax furnishes higher values than Burseracea opopanax.

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50. Sagapenum.

Gummi-resina Sagapenum.

Origin and Habitat.—Not accurately known; at any-rate, a Persian Umbellifera. Persia.

Chemical Constituents.—Resin soluble in ether, 56·8 per cent.; gum, 23·3 per cent.; water, 3·5 per cent.; impurities, 10 per cent.; ethereal sulphurous oil, 5·8 per cent. The pure resin contains: free umbelliferone, 0·11–0·15 per cent.; combined umbelliferone, 15·7 per cent.

of which about 40 per cent. is in the form of umbelliferone-sagaresinotannol ester. The sagaresinotannol has the formula $C_{24}H_{27}O_4OH$ (Hohenadel).

General Properties and Commercial Varieties.—

Dark brown masses, with numerous white lumps, of brittle consistence, turning soft and plastic in the hand. The smell faintly recalls galbanum, but also approximates to asafœtida. The ethereal solution gives a red-violet coloration with hydrochloric acid. Sagapenum is soluble in alcohol, ether, alkalis, and sulphuric acid. Formerly the principal commercial varieties were Persian sagapenum “in massa” and Levantine “in tears,” but at the present time the drug has almost entirely disappeared from the market.

Analysis. — Analytical data are practically non-existent; and it is only recently that the author and Mauch published a few contributions on the subject. The former examined sagapenum by exactly the same method as he applied to myrrh, bdellium, and opopanax, using the crude product instead of an extract. The *modus operandi* is as follows:—

(a) *Acid value, d.* (S.-Z. d.).—One grm. of the finely triturated sagapenum is taken, as an average sample, from a larger quantity, is suffused with 30 c.c. of distilled water and warmed for fifteen minutes under a reflux condenser. Fifty c.c. of strong alcohol are next added, and the whole boiled for fifteen minutes in the steam bath, still under a reflux condenser. When cold, the liquid is titrated with alcoholic $\frac{n}{2}$ potash and phenolphthalein, until a true red coloration is produced, the stronger alkali being used in preference to the decinormal on account of the sharper and quicker end reaction obtained. The volume (c.c.) of combined KHO multiplied by 28.08 gives the acid value.

(b) *Saponification value, h.* (V.-Z. h.).—A further 1 gm. average sample is suffused with 30 c.c. of water, left for half an hour, and then treated with 25 c.c. of alcoholic potash, after which it is boiled half an hour in the steam bath and under a reflux condenser, cooled, and titrated back after dilution with alcohol. The volume (c.c.) of consumed KHO multiplied by 28·08 gives the saponification value.

(c) *Ester value* (E.-Z.).—This is found by difference.

The author obtained the following values from the crude product :—

	I	II.
Acid value, d (S.-Z. d.) . . .	13·96	14·81
Ester value (E.-Z.) . . .	31·29	39·37
Saponification value, h. (V.-Z. h.)	45·25	54·18

Mauch found sagapenum to contain umbelliferon, and to dissolve, as a brown liquid, in 60 per cent. chloral hydrate. Like galbanum, sagapenum gives all the reactions for umbelliferon.

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51. Asafœtida.

Gummi-resina asafœtida (officinal in Germ. Pharm. III.).

Origin and Habitat.—*Ferula Scorodosma* and *F. Narthex*, Boiss. Persia.

Chemical Constituents.—Resin soluble in ether = fœrulaic asaresinotannol ester, 61·4 per cent.; free asaresinotannol ($C_{24}H_{33}O_4OH$), 0·6 per cent.; gum, 25 per cent.; ethereal sulphurous oil, 6·7 per cent.; vanillin, 0·06 per cent.; free fœrulaic acid, 1·28 per cent.; moisture, 2·36 per cent.; impurities, 2·5 per cent (Polasek).

General Properties and Commercial Varieties.—The *in massa* and *in lacrymis* varieties of asafœtida are

those now met with in commerce, the former being very impure, but the latter much purer. When fresh, the juice is white, though sometimes red or discoloured, with a strong smell of garlic; the external colour is dark violet, the flavour very sharp and persistently biting. As, in the case of ammoniacum and galbanum, the variety *in massa* is preferable to the other for pharmaceutical purposes, on account of its higher percentage of ethereal oil.

The most inferior kind, *Asafœtida petraea*, or “petrified asafœtida,” is a very impure mass, and should be rejected.

According to Dymock, three distinct kinds are recognised in the Bombay market, viz. *Abus ha herce* (from the port of Bunder Abbar, in the Persian Gulf), *Kanda haree*, and *Hingra*.

Whereas the first-named is derived from *Ferula alliacea*, Hingra is said to be the kind current in European commerce, the Persian asafœtida coming from *Scorodosma fœtidum*, and the Afghan from *Narthex Falconer*.

The very dear grade, “Hing from Abushaher” (in the province of Kerman), is said by Flückiger to be shipped in small quantities from Persian ports; and, according to Dymock, is adulterated with gum.

The present-day view, based on the researches of Holmes, is that all varieties presumably come from *Ferula Narthex*, Boiss.

Adulterants.—Inferior varieties, already exhausted by extraction, and containing over 5 per cent. of ash; African ammoniacum; extraneous resins; and vegetable residues.

Analysis.—Asafœtida has been found to contain a larger percentage of ash and impurities than any other member of the gum resins. Waage stated that residues of the parent plant, etc., are frequently present; Muter described varieties containing up to 70 per cent. (!) of stones; and Dymock

mentioned the great frequency of intentional adulterations with sand, gum, etc. In view of the high ash content, E. Dieterich advised using the purified product, and showed that the percentage of ash can be reduced from 46 per cent. to 18 per cent., and the percentage soluble in alcohol increased from 29 per cent. to 57 per cent. On this point, however, the remarks already made in the introduction to this present section apply. Whereas the German Pharmacopœia fixes 6 per cent. as the maximum permissible percentage of ash, the Dutch Pharmacopœia allows 20 per cent. of ash, the decision being based on the subjoined determinations:—

	Ash per cent.
Asafœtida pulv. I ^a	53·75
Do. in massa, extraf.	40·83
Do. in massa	45·32
Do. dep. pulv.	50·43
Do. in lacrymis	2·08

Both the above limits appear to err, the Dutch on the side of lenience, the German on the side of stringency; and a medium course (10 per cent.) would be preferable.

J. N. Lloyd also occupied himself with the examination of asafœtida, his main attention being bestowed on adulterations with colophony or white turpentine, which are readily detected by their higher acid values. The samples examined, however, proved free from either admixture. The dry, hard drug “in tears” exhibits the highest acid value (61·9–68·2),¹ that of the semi-fluid kind being much lower (31·1–40·4). The ordinary commercial grade contains an enormous pro-

¹ These data do not justify the assumption that “tears” give a higher acid value all round than “mass,” the contrary being usually the case with ammoniacum and galbanum, so that no general rule appears possible. See the results found by Beckurts and Brüche (lower down), where the “tears” actually gave the lowest acid values.

portion of ash, the average being 16–20 per cent., and in individual instances attaining 50 per cent. The purest “tears,” however, leave but very little ash (1·78–2·55 per cent.), and furnish about 76 per cent. of matters soluble in alcohol. It is stated that *asafoetida depurata* alone should be employed for officinal uses. Apparently it is almost impossible to find in the American market a quality complying with the requirements of the United States Pharmacopœia, which prescribes a 60 per cent. solubility in alcohol.

Morner and Fristedt detected a very subtle adulteration of *asafoetida in lacrymis*. Only 5 per cent. of the total drug was pure; whilst, of the remainder, 5 per cent. consisted of small fragments of gypsum, the rest being pieces of alabaster coated with a thin layer of *asafoetida*, the proportion of which varied from 7 per cent. in most of the lumps to 20 per cent. in others.

Hirschsohn examined numerous specimens, and found the following degrees of solubility in petroleum ether:—

	Dried at 17° C.	at 120° C.
1. <i>Asafoetida in granis</i>	8·25	3·27
2. Do. do.	5·33	2·12
3. Do. do.	1·85	1·02
4. Do. in massis	10·88	3·44
5. Do. do.	1·50	1·01
6. Do. in granis	7·40	1·73
7. Do. petræa I.	2·00	1·01
8. Do. do. II.	3·20	2·21
9. Do. ordinary	5·10	3·20
10. Do. from Bombay	11·44	4·65
11. Do. from Hanbury	13·45	3·44

He remarks: “The percentage soluble in petroleum ether should amount, in the case of an ordinary good commercial sample of *asafoetida in granis*, to at least

7 per cent., and to 5 per cent., at least, of the variety *in massis*. The quantity of matter volatilising at 120° C. should be not less than 5 per cent. and 3 per cent. respectively, referred to the total weight of the drug. A good quality of Indian asafœtida should give up not less than 11 per cent. to petroleum ether, and the residue should not lose less than 6 per cent. on being heated at 120° C."

Kremel found (usual method)—

		I.	II.
From extract	Resin per cent. . . .	72·1	35·6
	{ Acid value, d. (S.-Z. d.)	26·8	54·8
	{ Ester value (E.-Z.) . .	145·2	182·1
	{ Sapon. val., h. (V.-Z. h.)	172·0	236·9

E. Dieterich found (same method)—

		Asafœtida.			
		<i>Cruda.</i>		<i>Depurata.</i>	
From extract	{ Acid value, d. (S.-Z. d.)	11·20-	55·00	23·52-	82·30
	{ Ester value (E.-Z.) . .	110·60-	129·00	82·30-	101·70
	{ Sapon. val., h. (V.-Z. h.)	121·80-	184·00	164·60-	171·70
	Ash per cent.	6·5 -	66·05%	1·60-	4·40%
	Sol. in 90 percent. alcohol	15·43-	59·66%	66·00-	78·83%

Beckurts and Brüche found (same method)—

		From extract				
Asafœtida.	Sp. gr.	Ash %	Sol. in Alcohol %	Acid Value, d. (S.-Z.d.).	Ester Value (E.-Z.).	Sapon. Value, h. (V.-Z. h.).
In massa .	1·730	1·2	36	40	141	181
In depurata	1·290	3·1	43	29	180	209
	1·280	2·9	50	31	183	214
In massa .	1·293	5·0	58	43	162	205
In granis .	1·316	5·8	44	27	179	206

and stated that the presence of turpentine can be reliably detected by the acid value.

As in the case of ammoniacum and galbanum, the present author has worked out a method for asafoetida which permits the use of the crude product instead of extract, and determines the acid value by back titration. This last-named process is applicable here, because asafoetida is difficult to saponify, cold or fractional saponification being impracticable. In back titration, the drug can be used direct without previous conversion into a solution or extract; and, moreover, the intermediate gradations of colour-change, which impede the reading of the end-point in direct titration, are here lacking.

The method is performed as follows:—

(a) *Acid value, ind.* (S.-Z. ind.).—One grm. of asafoetida is suffused with 10 c.c. each of alcoholic and aqueous $\frac{n}{2}$ potash, and left to stand in a stoppered glass flask for twenty-four hours at room temperature. After dilution with 500 c.c. of water, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein, the volume (c.c.) of KHO consumed multiplied by 28.08 giving the acid value.

(b) *Saponification value, h.* (V.-Z. h.).—A 1 grm. average sample of the finely triturated drug is suffused with 25 c.c. of alcoholic $\frac{n}{2}$ potash and boiled for one hour under a reflux condenser. At the end of that time 200 c.c. of alcohol are added, and, when cold, the whole is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of consumed KHO multiplied by 28.08 gives the saponification value, h.

(c) *Ester value.*—Found by difference, as usual.

(d) *Ash determination.*—Two grms. of substance are carefully incinerated, and calcined until found constant after cooling in a desiccator.

The examination of a number of commercial samples

furnished the author with the following values (in round figures):—

Acid value, ind. (S.-Z. ind.)	65- 80
Ester value (E.-Z.)	80-130
Saponification value, h. (V.-Z. h.)	120-185
Ash	1- 10 per cent.

Gregor and Bamberger obtained the following methoxyl values (M.-Z.):—

	I.	II.
Gregor	11.9	6.9
Bamberger	18.0	—

Kitt found the carbonyl value (C.-Z.) = 0.2.

(For the worth of these determinations see *Chem. Rev.*, 1898, No. 10; and for the Germ. Pharm. III. tests for asafœtida, see *Ph. C.*, 1899, No. 21.)

Mauch found that the gum and resin in asafœtida are soluble (and perfectly clear) in 10-15 parts of 60 per cent. chloral hydrate solution, and recommends this method for the detection of impurities. He says—

“This gum resin often coming into the market adulterated with sand, stones, etc., the estimation of the mineral constituents is rendered difficult. It is generally effected by incineration, as prescribed by the Germ. Pharm. III., the maximum permissible ash content being 6 per cent. Owing to the difficulty experienced in incinerating the gum resins, the determination may be made equally well, and with greater accuracy, by the aid of chloral hydrate, the drug being treated with 10-15 times its own weight of 60 per cent. chloral hydrate solution, whereupon all the gum and resin will slowly dissolve, leaving the mineral admixtures behind. When an insoluble residue is left, it is placed on a filter of known ash content, washed first with 60 per cent. chloral hydrate, and afterwards with a little alcohol, dried, calcined, and weighed.”

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52. Olibanum, or Incense.

Olibanum, Gummi-resina Olibanum.

Origin and Habitat.—*Boswellia Carterii*, *B. serrata*, and other Burseraceæ. The Somali coast.

Chemical Constituents.—Boswellic acid ($C_{32}H_{52}O_4$), free and combined as an ester with olibanoresenes ($C_{14}H_{22}O$)_n. Ethereal oil ($C_{16}H_{16}$)_n (pinene, dipentene, phellandrene). Gum, with arabic acid ($C_6H_{20}O_5$), bassorin, and bitter principle (Halbey).

General Properties and Commercial Varieties.—Small tear-shaped, brittle granules, of dull pale yellow colour, and covered with dust; only partially soluble in alcohol, ether, chloroform, or other solvents. When chewed, the drug breaks down to powder and then softens; the taste is rather bitter and aromatic.

Olibanum electum is the best and purest kind, *Olibanum in sortis* being less pure, and corresponding to the *in massa* quality of other gum resins.

The so-called "wild incense," *Olibanum silvestre*, is a pine resin which was formerly employed to adulterate the pure drug. Olibanum, from *Boswellia Freriana* and *B. sacra*, is identical with African elemi (*q.v.*), and is termed "Luban Matti." It should more properly be classed with the elemis and not with the incense group. The resins of other species of *Boswellia*, such as *B. papyrifera*, *B. thurifera*, *B. oblongata*,

and *B. socotrana* are similar to olibanum, but are not met with in commerce. Cayenne incense, from *Icica heptaphylla*, also belongs to the elemis.

The *Protium* species, such as *P. multiflorum* ("Paú de incenço = incense tree), furnish varieties of incense, or substitutes therefor. They are mostly consumed in the interior of Brazil, just as the incense from the Composita, *Flourensia thurifera*, is known only in Mexico.

Indian incense is also obtained from a species of *Boswellia* (*B. serrata*), and not, as formerly stated, from *Juniperus Phœnicia*, *J. thurifera*, or *Amyris Kafal*. According to Kosteletzky and Hirschsohn, the name "Indian" is due to the circumstance that the incense was brought to Europe in Indian vessels *via* Egypt and Arabia. The relatively good concordance of the analytical data, furnished by ordinary and Indian incense, indicates that they are identical.

Adulterants.—Colophony, wild incense, mastic, and sandarach.

Analysis.—Incense can be distinguished from mastic and sandarach by its odour when heated, its solubility, behaviour when chewed, and by its analytical constants (principally that, like amber, it gives saponification values which are not furnished by mastic or sandarach). Numerous analytical data have been published on olibanum.

Hirschsohn examined Arabian, Indian, and African incense, and found the percentage of extract soluble in petroleum ether to amount to 22·08–38·81 per cent. after drying at 120° C. He believes that, as already stated, all the different kinds are referable to the African commercial grade.

The presence of wild incense (pine resin) in olibanum is dealt with as follows in the *Südd. Ap.*, 1899, No. 12 :—

"After frequent agitation with water, and leaving at rest for two days, granular incense should leave a white,

saccharine mass of resinous constituents, the gum being completely dissolved, whereas an admixture of pine resin will be indicated by the presence of lustrous yellow granules, which may be estimated in an approximately quantitative manner by washing and drying."

Kremel found (usual method)—

	Resin per cent.	Acid Val., d. (S.-Z. d.).	Ester Val. (E.-Z.).	Sapon. Val., h. (V.-Z. h.).
Olibanum .	64.0	59.3	6.6	65.9
Do. .	72.1	46.8	41.0	87.8
Do. Indicum	67.0	50.3	60.5	110.8

From extract.

E. Dieterich found (same method)—

Acid value, d. (S.-Z. d.) . . .	45.40	} from extract.
Ester value (E.-Z.) . . .	71.60	
Saponification value, h. (V.-Z. h.)	117.00	

The present author has worked out a method which enables the natural olibanum to be used instead of an extract. The *modus operandi* is as follows:—

(a) *Acid value, ind.* (S.-Z. ind.).—One grm. of olibanum is suffused with 10 c.c. of alcoholic and 10 c.c. of aqueous $\frac{n}{2}$ potash, and 50 c.c. of benzine (sp. gr. 0.700). After standing twenty-four hours in a stoppered glass flask, and then adding 500 c.c. of water, the liquid is titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of combined KHO multiplied by 28.08 gives the acid value.

(b) *Saponification value, h.*—One grm. of the finely triturated drug is suffused with 20 c.c. of alcoholic $\frac{n}{2}$ potash, and boiled an hour under a reflux condenser, the liquid being then diluted with 100 c.c. of alcohol and titrated back with $\frac{n}{2}$ sulphuric acid and phenolphthalein. The volume (c.c.) of

combined KHO multiplied by 28.08 gives the saponification value.

(c) *Ester value* (E.-Z.).—This is found in the usual way, by difference.

(d) *Ash content*.—Two grms. of olibanum are carefully incinerated, and calcined until found constant after cooling in a desiccator.

The following values were obtained :—

		Acid Val., ind. (S.-Z. ind.).
1. Olibanum pulvis		{ 46.20
		{ 43.40
		{ 46.20
		{ 44.80
2. Do. in granis		{ 42.00
		{ 42.00
		{ 42.00
		{ 42.00
3. Do. naturale I.		{ 50.40
		{ 46.20
4. Do. do. II.		{ 44.80
		{ 46.20
		{ 42.00
		{ 43.30
5. Olibanum electum		{ 32.20
		{ 33.60
		{ 30.80
		{ 35.00

From these figures it is evident that the *electum* grade, being the purest, gives the lowest acid values, the *pulvis* form yielding the highest values; a circumstance which points to the adulteration of the latter kind (see also Gamboge).

The advantages of the new method, especially the acid value determination by back titration, consist in the first place in the non-necessity of preparing a solution—which

would only occasionally be possible with incense—secondly, in a better and more certain colour-change than in direct titration; and, finally, in the possibility of replacing extract by the natural product.

For the ester and saponification values, the author obtained these figures—

Ester value (E.-Z.)	110-170
Saponification value, h. (V.-Z., h.)	140-230
Ash	traces.

In examining the acid value as a means of detecting adulteration, the subjoined values were obtained:—

	Acid Val., ind. (S.-Z. ind.)—	
1. Olibanum + 10 % of dammar	47·60	47·60
2. Do. + 20 % do.	46·20	46·20
3. Do. + 10 % of sandarach	58·80	56·00
4. Do. + 20 % do.	58·80	57·40
5. Do. + 10 % of gallipot	65·80	65·80
6. Do. + 20 % do.	74·20	71·40

Although dammar cannot be detected by this means—and only by the ester and saponification values, which are thereby lowered—the values rise considerably in presence of adulteration with sandarach or pine resin. If either of these adjuncts be suspected it is advisable to omit the addition of water before titration, in order to avoid the decomposition of the colophony, or sandarach, soap thereby produced. Information on this point will be afforded by the Storch-Morawski reaction for colophony (*q.v.*).

The author also found the following degrees of solubility:—

In Alcohol	} partially soluble, leaving white amorphous residue.
Ether	
Benzine	
Carbon di-sulphide—	partially soluble; residue plastic.
Chloroform	} partially soluble.
Acetone	

In Glacial acetic acid	}	for the most part insoluble.
Benzol. . .		
Methyl alcohol	}	partially soluble.
Amyl do.		
Oil of turpentine		

Like dammar, amber, and copal, the solubility of olibanum is increased by heat and fusion.

Gregor and Bamberger obtained the following methoxyl values (M.-Z.) :—

Gregor	6·4
Bamberger	5·3

Kitt found the carbonyl value (C.-Z.) = 0·36. (On the worth of these determinations, see *Chem. Rev.*, 1898, No. 10.)

Mauch found that olibanum furnishes only a turbid solution with 60 per cent. chloral hydrate, some time being required for the liquid to clarify. The reason for this is, that the drug contains up to 7 per cent. of ethereal oil, which is only very slowly taken up by the above solvent.

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APPENDIX.

THE following additional particulars have in part been compiled during the time the book was in type, and also contain other supplementary matter:—

PART I.

Classification of Resins.—According to the most recently published report by Tschirch (Paper read before the Naturforscherversammlung—Meeting of the German Association of Natural Philosophy—at Munich, 1899), the following classification of the resinous bodies has been drawn up:—

1. *Resinotannol resins*—
 - (a) Benzoic acid resins.
 - (b) Umbellifer resins.
2. *Resene resins*—
 - (a) Droseraceæ resins.
 - (b) Dipterocarpeæ resins.
3. *Resinol resins*.
4. *Resinol acid resins*—
 - (a) Coniferæ resins.
 - (b) Cæsalpinoideæ resins.
5. *Glucos resins*.

PART II.

Canada Balsam.

Chemical Constituents.—By fractional separation from methyl alcohol (see *Schweiz. Wochenschr. f. Chem. u. Pharm.*,

1899, No. 44; and *Ph. Ztg.*, 1899, No. 77) Tschirch has recently succeeded in isolating, from the resin from *Abies Canadensis*, "crystalline" resinol acids, which stand in a certain relationship to abietic acid (Mauch) and pimaric acid (Vesterberg).

Copaiba Balsam.

Chemical Constituents.—Tschirch has succeeded in isolating from several copaiba balsams—by fractional saponification with ammonium carbonate, soda, etc. (see *l.c.*)—several hitherto unknown resin acids, *e.g.* a β -metacopaibic acid, from Maracaibo copaiba ($C_{11}H_{16}O_2$), differing from Strauss' metacopaibic acid, which is classed as α -metacopaibic acid; a para acid (I.) obtained from Para balsam by means of ammonium carbonate, which acid has the m.p. about $195^\circ C.$, but is not identical with Fehling's oxycopaibic acid; a para acid (IV.) isolated with soda. A new acid, to which the name of "gurjuresinol" is given, has also been isolated from Gurjun balsam; and illuric acid ($C_{14}H_{20}O_2$) has been isolated from West African Illurin balsam, and analysed.

Peruvian Balsam.

Chemical Constituents.—Whereas the cinnamein examined by Thoms consisted for the most part of cinnamic, benzyl ester with only a little benzoic benzyl ester, the Peruvian balsam (*i.e.* the cinnamein isolated therefrom) examined by Tschirch showed a converse ratio. Tschirch believes this variation to be due to irregularities in the method of collecting the balsam. (This point has already been referred to by the present author, on the basis of the irregular analytical results obtained by him.)

The myroxocarpin ($C_{48}H_{35}O_6$) formerly observed in white Peruvian balsam (as at one time met with in commerce), but afterwards unsuccessfully sought for, has again been found by Tschirch.

Analysis.—Caesar & Loretz made the following remarks in their report, dated October 1899:—"According to the researches of Fromme, it is necessary to the attainment of concordant results in the determination of cinnamein by parallel analyses that the amount of water employed for agitation should be strictly regulated, and—like the quantity of soda used—kept down to a minimum, since otherwise a not unimportant percentage of cinnamein is retained in the liquid. Particularly concordant values were obtained by Fromme, by using first 25 c.c., then 5 c.c. of 2 per cent. caustic soda, and then 2×5 c.c. of water for the agitation.

"In the present state of our knowledge of the balsams, the following points seem to us of importance in the testing of Peruvian balsam:—

"1. Limiting the sp. gr. to 1.136–1.150.

"2. The nitric acid test with benzol-free benzene, in presence of five drops of HNO_3 (sp. gr. 1.38). The coloration of the entire mass when the reaction has set in should be yellow to brownish yellow.¹

"3. The cinnamein determination by the Thoms method, with the foregoing slight modification, should yield at least 60 per cent.

"4. The identification of the cinnamein by the ester value, which should be under 235."

¹ In the author's opinion, it is a pity that prominence should be again given to this unreliable test in face of the really useful quantitative tests. In view of the failure of this nitric acid reaction with the pure drug, the only course that can be advised is to omit it altogether, more especially in view of the efficacy of the quantitative reactions already given in the present work (see Peruvian Balsam).

Acaroid Resin.**Analysis.**—M. Bamberger found—**I. *Yellow Acaroid*—**

	I.	II.	From
Acid value, d. (S.-Z. d.) . . .	132	133	} purified resin.
Saponification value, h. (V.-Z. h.)	220	225	
Methoxyl value (M.-Z.) . . .	27.66	28.97	crude resin.
Methoxyl value (M.-Z.) . . .	34.73	—	purified resin.

II. *Red Acaroid*—

	I.	II.	From
Methoxyl value (M.-Z.) . . .	60.3	60.9	crude resin.
Methoxyl value (M.-Z.) . . .	71.2	—	purified resin.
Carbonyl value (C.-Z.) . . .	0.97	—	purified resin.

Owing to the dark colour of the red resin solution, the acid and saponification values could not be determined.

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Amber.

General Properties and Commercial Varieties.—The so-called “pressed amber,” or “ambroid,” is prepared in plates, by placing small assorted pieces of amber in cast-steel moulds at a temperature of 200–250° C., and exposing them to a pressure of about 400 atmos.

The waste pieces, from $\frac{1}{24}$ to $\frac{1}{4}$ inch diameter, are used up for making varnish, amber resin, and succinic acid.

Resina Pini.

General Properties and Commercial Varieties.—The ordinary pitch, the boiled and hardened turpentine-free conifer resin, is met with in commerce as yellow, or white, Burgundy

pitch, shoemakers' wax, and brewers' pitch; the last-named variety melting readily to a thin fluid. Mannite pitch is a very impure form of brewers' pitch. Asphalt is fossilised pitch.

Analysis.—J. Brand states that brewers' pitch is generally loaded (up to 13·12 per cent.) with mineral matters. The so-called mannite pitch is a kind which contains up to 32·12 per cent. of ferruginous compounds (iron glance), and is therefore unsuitable for brewers' use.

Thapsia Resin.

General Properties and Commercial Varieties.—Leroux (*Bulletin Commer.*, 1899, 27, p. 417) reports on the extraction and dangerous nature of this resin (agreeing with the author's remarks, *q.v.*), and gives the following additional particulars as to its properties:—

“*Thapsia garganica* is a large umbellifer, indigenous to Algiers, and is chiefly found in the uplands, associated with *T. decussata*. The active blistering principle is mainly found in the root skin of the plant. The alcoholic extract of the central portion of both varieties is insoluble in water, and that from the bark of *T. garganica* is, for the most part, insoluble in this liquid. The green leaves induce redness when applied to the skin, and great care is necessary in extracting the resin from the roots of *T. garganica*; so that the outer skin of the fresh roots has to be taken off under water (see the author's method under Thapsia resin). The resin is generally obtained by distilling the preparation resulting from the treatment of the more or less pulverised rind with 80–90 per cent. alcohol. The preparation is frothy and fluorescent, owing to the presence of saponin, which is difficult of removal. Benzol is a better solvent

of the resin than alcohol, and gives a better product. On evaporation, the benzol preparation leaves the resin as a brown, transparent, pasty mass; whereas the alcoholic preparation yields an opaque, pale mass, of the consistence of honey, which, when treated with benzol, is converted into the resin. Thapsia resin is insoluble in ethereal oils or petroleum benzine."

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DYERS' MATERIALS: An Introduction to the Examination, Evaluation and Application of the most important Substances used in Dyeing, Printing, Bleaching and Finishing. By PAUL HEERMAN, Ph.D. Translated from the German by ARTHUR C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.). With Two Plates, containing Twenty-four Illustrations. Crown 8vo. 150 pp. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s; strictly net.

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